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CIX. *The β-Rays associated with Scattered X-Rays.*

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[Plates XIX.–XX.]

I. INTRODUCTION.

C. T. R. WILSON † and others ‡, using the cloud method, have shown that the β-ray tracks produced in air by relatively hard X-rays are of two distinct types, distinguished chiefly by their relative lengths. The types are: (*a*) long tracks due to electrons ejected with initial kinetic energy comparable to a quantum of the incident radiation: these tracks are due to the photoelectrons ejected from atoms which have each *absorbed* one quantum of the primary X-rays; (*b*) tracks of very short range which have been associated with the *scattering* of the incident X-rays, A. H. Compton § having shown that such tracks were a necessary consequence of his quantum theory of scattering. According to this theory, a single electron may scatter a single quantum of X-rays, the electron as the result of the encounter acquiring momentum equal to the vector-difference

* Communicated by Prof. W. L. Bragg, F.R.S.

† C. T. R. Wilson, Proc. Roy. Soc. A, civ. p. 1 (1923).

‡ Bothe, *Zeit. f. Phys.* xvi. p. 329 (1923); Compton and Simon, Phys. Rev. xxv. p. 306 (1925).

§ Compton, Bull. Nat. Res. Coun. xx. p. 19 (1922).

between that of the quantum before and after scattering. If the energy thus acquired by the electron is sufficiently large, it will leave the atom to which it is bound and give rise to a short β-ray. These are the rays which on the quantum theory of scattering are identified with the above-mentioned short tracks. The object of the work commenced in the experiments to be described in this paper, is to examine the number, length, and orientation of the *short* tracks produced in different gases by homogeneous X-rays of various known wave-lengths, and to compare the results with the requirements of the quantum-scattering theory of their origin. The present paper * will deal mainly with the number of short tracks in the gases oxygen, nitrogen, argon, and hydrogen, for X-rays of a few different wave-lengths. It is hoped later to extend the results to X-rays of shorter wave-length and it will then be possible to discuss the question of the length and orientation of the short tracks. During the progress of the work Compton and Simon † have published the results of a series of experiments on the β-ray tracks produced in air by approximately homogeneous X-rays, using the Wilson method. The results of their experiments bear out the quantum scattering theory of the origin of the short tracks, though they can hardly be considered as a very adequate test of the theory for the following reasons:—(1) The total number of tracks examined is small and it is obviously desirable to examine a large number, since the relation to be tested is a statistical one. (2) According to the theory the relative number of the two types of tracks varies approximately as $1/\lambda^3$, where λ is the wave-length of the incident X-rays. It is therefore of the highest importance that the wave-length of the X-rays should be accurately known, whereas in Compton and Simon's experiments the rays were only approximately homogeneous. In the present experiments the probable errors arising from the two above-mentioned causes have been very considerably reduced. In the first place about 4000 tracks have been counted involving the examination of more than 300 pairs of stereoscopic photographs, and secondly, we have used the crystal reflexion method to obtain a very homogeneous beam of X-rays of accurately known wave-length.

* An account of some of the observations given in this paper has already been published by the authors in the Memoirs of the Manchester Literary and Philosophical Society, No. 1, vol. lxx., 13th Oct. 1925.

† Compton and Simon, Phys. Rev. xxv. p. 306 (1925).

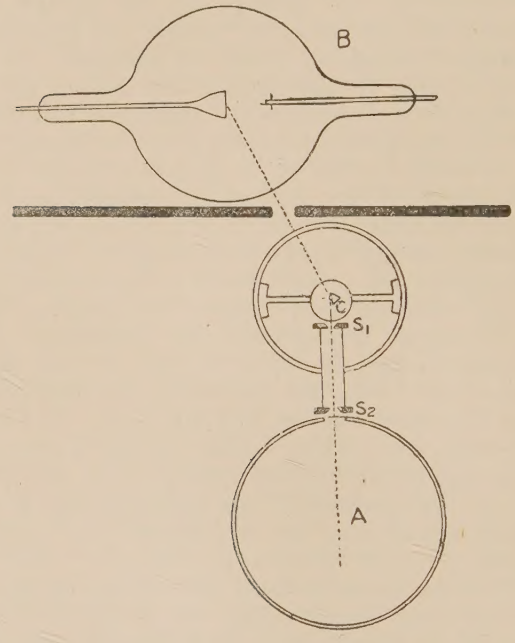
II. Experimental Arrangement.

The cloud-expansion apparatus used in the present investigation is of the well-known Wilson pattern and needs no further description. It is adapted so that different gases can be introduced into the cloud-chamber. The source of X-rays is a Coolidge tube excited by the discharge from Leyden jars maintained at a high potential from a Wimhurst machine. A second battery of Leyden jars, discharged through a mercury spark-gap, provides the illuminating "flash." The intervals between the expansion of the gas in the cloud-chamber, the passage of the X-rays, and the illuminating flash are carefully "timed" by trial until clear photographs of the β-ray tracks are obtained. In all cases stereoscopic pairs of photographs are taken, the camera lenses being Beck Isostigmars of maximum aperture f. 5·8. Imperial Eclipse plates have been found satisfactory.

In a quantitative study of the β-rays produced by a beam of X-rays it is of the greatest importance, as previously pointed out, that the rays used should be as nearly as possible homogeneous and of known wave-length. This has been done throughout the present series of experiments by using the X-rays reflected from a crystal at a known "setting." The experimental arrangement for obtaining a beam of homogeneous X-rays is shown in fig. 1. The slits S_1 S_2 which limit the beam that can enter the cloud-chamber A (through the mica window W) are fixed. The crystal C can be rotated, and for any definite setting X-rays of wave-length corresponding to that setting only, can enter the chamber A. The position of the Coolidge tube B (which is enclosed in a lead box) can be adjusted for any setting of the crystal C till a reflexion is obtained. The "homogeneity" of the beam obtained will depend on the width of the slits and their distance apart and to a certain extent on the nature of the crystal used. In sifting out some particular wave-length from the general radiation from the Coolidge tube, there is one other point to remember. For any setting θ of the crystal with respect to the fixed slits all wave-lengths (provided they are *present* in the radiation from the tube) which satisfy the relation $n\lambda = 2d \sin \theta$ may be reflected into the cloud-chamber. Thus we may get wave-lengths λ, $\lambda/2$, $\lambda/3$ ... corresponding to 1st, 2nd, 3rd order reflexions, the relative intensities of the different orders depending on the crystal used. In the earlier experiments in this work a rocksalt crystal and moderately wide slits were used, giving the wave-length to approximately ·05 Å.

Using the general radiation from a tungsten Coolidge tube and the rocksalt crystal, series of photographs were taken of the β-ray tracks produced in air by X-rays of wave-lengths ·57 Å and ·35 Å. (The results are tabulated later.) The rocksalt crystal was then replaced by a *diamond* in order to eliminate the possibility of a 2nd order reflexion. Although the intensity of the 2nd order reflexion in the case of rocksalt is only about one-fifth that of the first order, a few

Fig. 1.



photographs were obtained in which there were observed β-ray tracks produced by X-rays of wave-length corresponding to the higher order reflexion. In the case of the diamond there is practically no 2nd order reflexion from the [1. 1. 1] face, and the excitation of rays corresponding to higher orders is prevented by control of the potential applied to the tube. In general it is undesirable to use this latter control to prevent the 2nd order reflexion, as the lowering of the potential to the necessary value interferes too much with the output of X-rays. In the final arrangement used, the slits were 1/5 mm. wide and 10 cm. apart, and

the wave-length of the beam of X-rays entering the cloud-chamber was known to ·01 Å. With this arrangement about 250 stereoscopic pairs of photographs have been taken, using the Kα (·614 Å) and Kβ (·545 Å) radiations from a rhodium Coolidge tube and the Kα (·709 Å) radiation from a molybdenum tube.

The tracks produced by the above rays in the following gases have been examined:—oxygen, nitrogen, argon, hydrogen, and a mixture of hydrogen with a known small percentage of argon. The gases used were supplied commercially and were not specially purified. In the cases of the oxygen and nitrogen this is relatively unimportant, but in the case of the *argon* allowance had to be made for the relatively large proportion of nitrogen (about 15 per cent.) which it contained. There was no evidence of an appreciable amount of impurity in the hydrogen.

III. Examination of Photographs.

A few typical photographs have been reproduced in Plates XIX. and XX. and show the nature of the β-ray tracks in different gases and for different wave-lengths of X-rays. It is seen that the tracks in all the photographs can be divided into the two classes previously mentioned, viz. one class consisting of short tracks and the other of tracks with a length of the order of a cm. Though the short tracks only appear as "spots" on the plates, it is possible by simple tests to ascertain their genuine nature and thus avoid confusing them with spots which sometimes appear on the plates but which are not photographs of β-ray tracks.

IV. Distribution of Short Tracks with respect to the Origins of the Long Tracks.

In an account of the nature of the β-rays produced by X-rays, C. T. R. Wilson* describes paired tracks in which one of the pairs is a long track and the other a short track, the origins of the tracks being slightly separated. This is stated to occur only with rays of wave-length less than about ·5 Å. Though this excludes most of the present experiments, observations in certain cases have been made on the distribution of the short tracks in order to see if there is any tendency for them to occur near the origins

* C. T. R. Wilson, Proc. Roy. Soc. A, civ. p. 1 (1923).

of long tracks. A further reason for making these observations is to test the accuracy of the procedure adopted in counting the total number of short tracks on a plate. In the case of a spot which is within a fraction of a mm. of the origin of a long track, it is very difficult to ascertain with certainty whether it is a part of the long track or a separate short track. In the procedure we have adopted the number, N'_R, of short tracks *excluding* those within a mm. of the origin of long tracks is first counted. The number, N_{R1}, of short tracks excluded is then calculated on the assumption that the short tracks are randomly distributed. The sum, $N'_R + N_{R1}$, then gives the total number N_R, of short tracks on the plate. A spot at a distance greater than a mm. from the origin of a long track is not part of that track and is certainly a photograph of a separate short β-ray track. There is therefore little or no uncertainty concerning these, and the distribution of short tracks on the plates has been tested by counting the number, $N_{R1.2}$, of short tracks at distances between 1 and 2 mm. from the origins of long ones, as well as counting the total number of short tracks outside a mm. range of the long ones. The beam of X-rays in the cases investigated was in the form of a thin sheet approximately normal to the axis of the camera, so that the distribution of points in the beam reduces to that of points on a plane. The theoretical relation of $N_{R1.2}$ to N'_R on the assumption that the short tracks are randomly distributed will now be considered.

Let A = area in sq. mm. of the beam of X-rays on the plate.
N_P = number of long tracks.
N_R = *total* number of short tracks.
N'_R = number of short tracks, at distances on the plate greater than 1 mm. from origins of long tracks.
N_{Ra} = number of short tracks within a distance "a" mm. of origins of long tracks.

Then total area of circles of radius a drawn round origins of long tracks $= N_P \cdot \pi a^2$.

Average number of short tracks per mm.^{2} $= N_R/A$.

Assuming a random distribution of short tracks,

$$N_{Ra} = \left[\frac{N_R}{A}\right] \times N_P \cdot \pi a^2, \quad . \quad . \quad . \quad . \quad (1)$$

and for a series of photographs,

$$N_{Ra} = \frac{\pi a^2}{A} \cdot \Sigma N_R \cdot N_P. \quad . \quad . \quad . \quad . \quad . \quad (2$$

The possibility of two circles overlapping one another or of a circle extending outside the boundary of the beam has been neglected. To allow for the former the expression for N_{Ra} must be multiplied by the factor $\left[1-\frac{(N_P-1)\pi a^2}{2A}\right]$ and to allow for the latter by the factor $[1-4a/3\pi t]$, where t is the width in mm. of the approximately rectangular beam. It can readily be shown that the corrected expression for N_{Ra} (making certain approximations) is given by

$$N_{Ra}=\frac{\pi a^2}{A}\left\{1-\frac{4a}{3\pi t}\right\}.\Sigma N'_R.N_P.\left\{1-\frac{\pi.N_P}{2A}.(a^2-2)\right\} \quad . \quad . \quad . \quad (3)$$

In the experiments made with diamond as the reflecting crystal,

$$A=760 \text{ mm.}^2, \qquad t=8{\cdot}5 \text{ mm.}$$

On substituting these values in (4) we find that

$$N_{R1.}={\cdot}0040\{\Sigma N'_R.N_P+\Sigma N'_R.N_P^2/480\} \quad . \quad . \quad (4)$$

$$N_{R1.2.}={\cdot}015\{\Sigma N'_R.N_P-\Sigma N'_R.N_P^2/240\} \quad . \quad . \quad (5)$$

The results of the examination of a number of plates are given in Table I.

TABLE I.

Gas.	Wave-length in Å.	$N_{R1.2}$.		N'_R (obs.).	N_{R1} (calc.).	$N_R=N'_R+N_{R.1}$
		Calculated.	Observed.			
Oxygen	·709	5	3	24	2	26
„	·614	30	37	114	15	129
„	·545	11	10	105	4	109
Nitrogen *a*...	·614	11	19	89	4	93
„ *b*...	·614	27	33	117	13	130
	·545	9	5	106	3	109
	Total	93	107			

The first and second columns give the gas traversed and the wave-length of the X-rays. The *calculated* numbers $N_{R1.2}$ of tracks at a distance between 1 mm. and 2 mm. from the origins of long tracks are given in column (3) and in column (4) the numbers actually observed are given. The agreement between the calculated and observed values of $N_{R1.2}$ is seen to be fairly good, the observed values in some

cases being less than the calculated probable values and in others greater. Since the calculated values are based on the assumption that the short tracks are randomly distributed, the agreement with the observed values shows that the assumption of such a distribution is justified, at least in the cases of short tracks produced at distances greater than 1 mm. from the origins of long tracks in the gases oxygen and nitrogen, at pressures of about 60 cm., and for X-rays of wave-lengths ·545 Å, ·614 Å, and ·709 Å respectively. If there is any tendency for short tracks to occur near the origins of long ones for X-rays of these wave-lengths (as pointed out by Wilson for slightly harder X-rays), then they must be produced within a mm. of the origins of the long tracks.

In the sixth column of Table I. are given the calculated values of N_{R1} which, when added to the values of N'_R of column (5), give the total number of short tracks N_R *. These are given in the last column of the Table and are the values used in the later discussion of the number of short tracks.

V. The Ratio of the Number of Short Tracks to the Number of Long Tracks.

Before giving the results which have been obtained in connexion with the relative number of the short and long tracks, the theoretical values of this ratio on the basis of Compton's quantum scattering theory of the origin of the short tracks will first be considered.

Calculation of N_R/N_P *on Compton's Theory.*

Compton and Hubbard † showed that since on the quantum theory each scattered quantum of X-rays is associated with a recoil electron, and each absorbed quantum with a photo-electron, then the ratio of the number of recoil electrons to the number of photo-electrons, is equal to the ratio of the number of scattered quanta to the number of absorbed quanta, *i. e.* is equal to the ratio of the scattering coefficient,

* Clearly this statement is incorrect if there are more *short* tracks within a mm. range of the long tracks than is consistent with a random distribution. However, such additional tracks would represent a different phenomenon from that which operates in the production of the class of short tracks which are randomly distributed, and therefore such tracks do not concern us here.

† Compton and Hubbard, Phys. Rev. xxiii. p. 448 (1924).

σ, to the absorption coefficient, τ. In this calculation of N_R/N_P the possibility that a scattered quantum may not give sufficient energy to the scattering electron to enable the latter to leave the atom is neglected. To allow for this possibility it is necessary to multiply σ/τ by a factor f, where f represents the fraction of scattered quanta which give the required energy to the scattering electron. The ratio N_R/N_P is then given by

$$\frac{N_R}{N_P} = f \cdot \frac{\sigma}{\tau}.$$

f depends on the wave-length of the X-rays and on the binding energies of the electrons, and its value will be calculated in an Appendix at the end of the paper *. In order, therefore, to determine the theoretical values of N_R/N_P, we require to know the values of σ/τ, and for this purpose the results obtained by C. W. Hewlett † have been assumed. Hewlett has determined the total mass absorption coefficients of a number of light elements for homogeneous X-rays varying in wave-length from ·1 Å to 1·0 Å. According to his results the total mass absorption coefficient μ/ρ of an element of atomic number N and for radiation of wave-length λ is given by

$$\frac{\mu}{\rho} = KN^3\lambda^3 + \frac{\sigma}{\rho},$$

where σ/ρ is the mass scattering coefficient, the term $KN^3\lambda^3$ representing the true mass absorption coefficient τ/ρ. For oxygen, Hewlett's value of K is $5{\cdot}71 \times 10^{-3}$ and σ/ρ is ·165. There is no evidence in Hewlett's results to show that K is different for nitrogen though he gives it a slightly different value, and for nitrogen the same values of K and σ/ρ have been used as in the case of oxygen. The values of K and σ/ρ assumed for argon are $5{\cdot}87 \times 10^{-3}$ and ·177 respectively, being intermediate between the values given by Hewlett ‡ for aluminium and iron. From these values, σ/τ for any of these gases and any wave-length can be obtained. In some of the experiments mixtures of gases have been used, and for such mixtures the theoretical value of N_R/N_P is given by

$$\frac{N_R}{N_P} = \frac{\Sigma f n \sigma}{\Sigma n \tau},$$

where n denotes the relative number of atoms of which the

* See Table V. for values of "f."

† C. W. Hewlett, Phys. Rev. xvii. p. 284 (1921).

‡ Hewlett's values of K and σ/ρ for aluminium are $5{\cdot}71 \times 10^{-3}$ and ·173, and for iron $6{\cdot}03 \times 10^{-3}$ and ·180.

absorption and scattering coefficients are τ and σ respectively. This completes the data necessary for the evaluation of the theoretical values of N_R/N_P, and the results obtained and shown in Table II. will now be considered.

TABLE II.

Gas.	Wave-length in Å.	No. of stereoscopic pairs of plates examined.	N_P.	N_R.	$\frac{N_R}{N_P}$.	$\frac{\sigma}{\tau}$.	f.	Theoretical value of $N_R/N_P = \sigma/\tau \times f$.
Oxygen.....	·709	22	205	26	·127	·174	·816	·142
Oxygen.....	·614	34	608	129	·212	·268	·843	·226
Oxygen.....	·545	50	358	109	·305	·383	·866	·332
Nitrogen ...	·614	46	722	223	·309	·400	·850	·340
Nitrogen ...	·545	34	202	109	·540	·572	·876	·501
†Argon	·614	10	209	7	·033	·030	·69*	·021
†Argon	·545	9	139	4	·029	·043	·73*	·031
Air	·57	37	454	153	·337	·372	·865*	·322
Air	·35	11	83	139	1·67	1·57	·94*	1·48

† Argon conta ned 15 per cent. of nitrogen.

* f in these cases $= \frac{\Sigma f n \sigma}{\Sigma n \sigma}$.

The first two columns in Table II. give the gas in the cloud-chamber and the wave-length of the radiation. In the fourth column are given the numbers, N_P, of long or photo-electron tracks produced, and in the fifth column the numbers, N_R, of short tracks, whilst the third column gives the numbers of stereoscopic pairs of photographs examined in each case. The ratios of N_R to N_P are given in column (6). The theoretical values of this ratio, calculated from the values of σ/τ given in column (7) and the values of "f" in column (8), are given in the last column. It will be seen from the Table that the difference between the observed and theoretical values of N_R/N_P (except in the case of argon, where the probability error is large as there are very few short tracks) is in no case greater than 13 per cent., the average difference being 9 per cent. These differences are within the experimental errors involved in the determination of N_R/N_P, σ, and τ. The error in the observed value of N_R/N_P arises from the fact that only a limited number of tracks are counted, and it has been computed that the average error in the various cases, due to this, is about 7 per cent. ‡ The values of σ and τ for

‡ If n is the average number of tracks produced under given conditions, then the probability that r tracks be produced under these conditions is $n^r \times e^{-n}/r!$—this formula has been used in estimating the average error.

oxygen are, according to Hewlett, probably correct to 1 or 2 per cent. For nitrogen the possible error is more and may be as much as 7 or 8 per cent. The error involved in "f" is probably less than 1 per cent., as f only varies slowly with the quantities involved in its determination. It may be concluded from these estimates of the errors that the average difference of 9 per cent. between the calculated and observed values of N_R/N_P can be accounted for by experimental error. We thus see that the numbers of short tracks produced in the various cases included in Table II. agree within the error of experiment, with the numbers required by Compton's theory.

The Number of Short Tracks produced in Hydrogen.

The true absorption of X-rays by hydrogen is so small that, on Compton's theory, there should be a predominance of short tracks even when the ionizing rays are comparatively soft. Observations made on the tracks produced in hydrogen should therefore provide an additional interesting test of the theory. The absorption in hydrogen is, as already stated, very small and has in fact never been truly measured. In the Wilson method of observing the β-rays, water-vapour is essentially present in the cloud-chamber and the absorption due to this is large compared with the true absorption in hydrogen, and the latter can be neglected *. The amount of water-vapour present at ordinary temperatures is about 2 per cent., and according to the theory the ratio N_R/N_P should be about ten times greater than in the case of pure oxygen or nitrogen. Two series of photographs of the β-ray tracks produced in hydrogen by X-rays of wave-length ·614 Å have been taken, the two series corresponding to two different temperatures and therefore different percentages of oxygen atoms. The results of the two series of photographs are given in Table III.

Column (1) gives the relative numbers of hydrogen and oxygen atoms in the cloud-chamber, and columns (5) and (6) the observed and theoretical values of N_R/N_P. The agreement is satisfactory, the smaller value of the observed ratio being expected if there is any impurity in the hydrogen, as this would obviously increase the observed number of photo-electron tracks N_P. (This is shown by giving in the

* The effect of the water vapour on the theoretical value of the ratio N_R/N_P in the cases discussed in Table II. is quite inappreciable.

last column of the Table the theoretical number of photo-electron tracks expected in each case, which is seen to be less than the number observed). A further series of photographs of the tracks produced by X rays of wave-length ·614 Å were taken when a small percentage of argon was introduced into the hydrogen filled cloud-chamber.

TABLE III.

Proportion of hydrogen and oxygen atoms in cloud-chamber.	λ in Å.	N_P.	N_R.	$\frac{N_R}{N_P}$.	Theoretical value of $N_R/N_P = f\sigma/\tau$.	Theoretical value of N_P calculated from columns (4) and (6).
Hydrogen : Oxygen =200 : 2·3 ...	·614	11	28	2·5	2·9	10
Hydrogen : Oxygen =200 : 1·47 ...	·614	21	73	3·5	4·4	16

The argon has the effect of increasing the number of photo-electron tracks and the value of N_R/N_P should be reduced. The photographs are interesting from another point of view, as they show the "tertiary" β-ray tracks produced by the K radiation of argon, as previously pointed out by Auger *. The absorption of a quantum of the incident radiation by an argon atom is accompanied by the ejection of a photo-electron (secondary β-ray) from that atom and the emission of the fluorescent K radiation of argon. The latter radiation subsequently ejects an outer electron from the same atom, and this electron has sufficient energy (about 4000 volts) to produce in the hydrogen atmosphere of the cloud-chamber a short β-ray track—the tertiary β-ray. In photograph 10 of Plate XX. these short tertiary tracks can be seen quite clearly starting from the same origin as the long photo-electron tracks.

The results showing the values of N_R, N_P, etc. for two different percentages of argon are given in Table IV.
The first column gives the relative number of atoms of hydrogen, oxygen, argon, and nitrogen in the cloud-chamber, whilst columns (5) and (6) give the observed and theoretical values of N_R/N_P. The agreement is again seen to be satisfactory. The last column shows the expected number of recoil tracks calculated from the numbers in columns (3) and (6).

* Auger, *Journal de Physique*, vi. No. 6, p. 205 (1925).

The results discussed in Tables II., III., IV., which cover a range of wave-lengths of the incident X-rays from ·35 Å to ·709 Å, and the gases oxygen, nitrogen, argon, and hydrogen, consistently show a remarkably good agreement between the observed values of N_R/N_P and the values which would be expected on the quantum theory of scattering, and constitute almost conclusive evidence in favour of that theory. It should be emphasized that the theoretical values

TABLE IV.

Composition of gas in cloud-chamber.	λ in Å.	N_P.	N_R.	$\frac{N_R}{N_P}$.	Theoretical N_R/N_P.	Theoretical values of N_R.
H : O : A : N =197·4 : 1·5 : 1·1 : ·4	·614	62	15	·24	·19	12
H : O : A : N =198·6 : 1·5 : ·58 : ·3	·614	71	28	·39	·34	24

of the ratio are based on the assumption that *all* the scattered radiation obeys the quantum theory of scattering. The spectrum of the scattered X-radiation has been shown to consist of a "modified" line and an "unmodified" one, the latter having the same wave-length as the primary radiation. The results of the present experiments show that either the unmodified radiation is produced according to the quantum theory or is present in the cases investigated in these experiments to an extent less than the experimental error, *i. e.* less than about 10 per cent. of the total scattered radiation.

Relation of the Short Tracks to the J *Phenomenon.*

According to C. G. Barkla* the Compton effect is a manifestation of the more general J phenomenon. One remarkable property of the J phenomenon is that quite frequently it does not occur at all though the conditions may be apparently unaltered from those under which it has previously been observed. This is, however, not a characteristic of the short β-rays observed in the present experiments. These rays are produced in all cases in which the strength of the primary beam is such as to provide a reasonable expectation of a short β-ray. Thus one of the main properties of the J phenomenon is *not* characteristic of the phenomenon of the production of short β-rays by X-rays.

* Phil. Mag. ser. 6, vol. l. p. 1133, Nov. 1925.

Neither has this property been observed in investigations of the change of wave-length due to scattering, but Barkla attributes this fact to the "duration" of the experiments. The non-manifestation of the property under the conditions of the present experiments cannot be similarly explained, since each experiment only involves a single instantaneous discharge through the X-ray tube and is therefore of the shortest possible duration. It should, however, be noted that each of the present experiments involves all directions of scattering.

*Calculation of "f" * †.*

The electron in scattering a quantum of X-rays acquires momentum equal to the vector difference between the momentum of the quantum before and after scattering. The energy gained by the electron is taken from the quantum which after scattering is characteristic of radiation of longer wave-length. The scheme is represented in figs. 2 *a* and 2 *b*.

Let λ=wave-length of incident X-radiation. Assume fraction p of the electrons in the scattering material possess orbital kinetic energy B^2 and ionization potential V. Consider quanta scattered through angles between θ and $\theta+d\theta$ by electrons belonging to this class, and let f_1 be the fraction of these which give recoil tracks. Consider an encounter in which the velocity of the electron before scattering makes an angle ϕ with the momentum communicated to it by the quantum (fig. 2 *b*).

We have

$$M_1^2=\left(\frac{h}{\lambda}\right)^2+\left(\frac{h}{\lambda+d\lambda}\right)^2-2\cdot\frac{h}{\lambda}\cdot\frac{h}{\lambda+d\lambda}\cdot\cos\theta. \quad . \quad (1)$$

* Jauncey (Phys. Rev. xxv. p. 314, 1925 and xxv. p. 723, 1925) has made calculations on the relative intensities of the modified and unmodified scattered radiations: in those cases it is only necessary to consider radiation scattered in one direction, whilst in the problem under consideration it is necessary to take into account the total scattered radiation.

† This calculation of "f" was first given by the authors in a paper read before the Manchester Lit. and Phil. Soc. in October 1925. In the Physical Review for the same month Jauncey also pointed out the necessity for the "f" correction. Jauncey assumed that a recoil electron, after escaping from the parent atom, must have an amount of energy at least equal to about 650 volts, before it can be detected by the cloud method. He gives corrected values of N_R/N_P for air in the cases investigated in Compton and Simon's experiments (*loc. cit.*). The cloud method is, however, capable of showing individual ions, and accordingly in the present work it is assumed that the ejection of an electron from an atom (no matter how small the surplus energy) will be recorded.

The energy gained by the electron is $(M^2 - M_2^2)/2m$, where m is the mass of the electron, and if it is able to leave the atom, we have

$$\frac{1}{2m}(M^2 - M_2^2) > V. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Fig. 2 *a*.

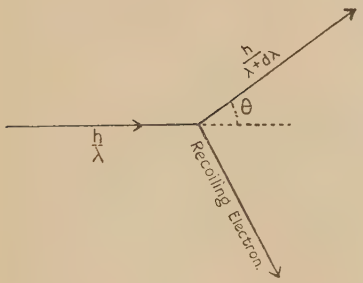
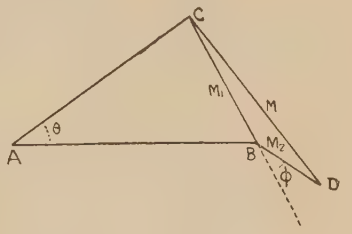


Fig. 2 *b*.



AB represents the momentum h/λ of the incident quantum.
AC „ „ $h/\lambda + d\lambda$ of the scattered quantum.
CB „ „ M_1 communicated to the electron.
BD „ „ M_2 of the electron *before* scattering.
CD „ „ M of the electron *after* scattering.
(ABC and CBD are not necessarily in the same plane.)

There are three cases to consider:

(*a*) The inequality (2) may be satisfied by all values of ϕ between 0 and π, in which case $f=1$.

(*b*) It may be satisfied by no values of ϕ, in which case $f=0$.

(*c*) It may be satisfied by some but not all values of ϕ.

In case (*c*) there exists a value, ϕ_c, of ϕ which is such that (2) is satisfied by all values of ϕ less than ϕ_c. When $\phi = \phi_c$, the energy communicated to the electron is just sufficient to eject it from the atom, so that ϕ_c is the value of ϕ which satisfies

$$\frac{1}{2m}(M^2 - M_2^2) = V. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From fig. 2 *b*,

$$\cos\phi = \frac{(M^2 - M_2^2 - M_1^2)}{2M_1M_2}.$$

So that from (3),

$$\cos\phi_c = \frac{2mV - M_1^2}{2M_1M_2}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When $\phi=\phi_c$, the energy, $h/\lambda-h/\lambda+d\lambda$, lost by the quantum is V, and as V for light elements is small compared with h/λ, equation (1) becomes

$$M_1^2=2m\psi^2\sin^2\theta/2,$$

where

$$\psi=\sqrt{\frac{2}{m}}\cdot\frac{h}{\lambda}\left[1-\frac{V\lambda}{2hc}\right].$$

Substituting this value of M_1 in (4) and replacing M_2 by $B\sqrt{2m}$, we have

$$\cos\phi_c=\frac{1}{2}\cdot\frac{V}{\psi B\sin\theta/2}-\frac{1}{2}\frac{\psi}{B}\sin\frac{\theta}{2}.$$

Since the direction of scattering is independent of the motion of the scattering electron (the latter being for light elements almost negligible compared with the velocity of light) the value of the fraction f_2 of electrons for which $\phi<\phi_c$ is given by

$$f_2=\frac{1-\cos\phi_c}{2}=\frac{1}{2}+\frac{1}{4}\frac{\psi}{B}\sin\frac{\theta}{2}-\frac{1}{4}\frac{V}{\psi B\sin\theta/2}. \quad (5)^*$$

There will in general be two values θ_1 and θ_2 of θ, such that the values of θ less than θ_1 belong to case (b), the values of θ between θ_1 and θ_2 to case (c), and the values of θ between θ_2 and π to case (a). Hence in the region defined by $0<\theta<\theta_1$, $f=0$, in the region defined by $\theta_1<\theta<\theta_2$, f is given by (5), and in the region defined by $\theta_2<\theta<\pi$, f is unity. The value of θ_1 is given by (5) when f_2 is put equal to zero. The value thus obtained is given by

$$\sin\frac{\theta_1}{2}=\frac{\sqrt{B^2+V}-B}{\psi}=\alpha, \text{ say.} \quad . \quad . \quad . \quad (6)$$

If there are no values of θ which make f_2 unity then $\theta_2=\pi$, and this is the case if $\psi^2-2\psi B-V<0$.

If $\psi^2-2\psi B-V\geqslant 0$, θ_2 is given by

$$\sin\frac{\theta_2}{2}=\frac{\sqrt{B^2+V}+B}{\psi}=\beta, \text{ say.} \quad . \quad . \quad . \quad (7)$$

In the case of light elements the intensity of scattering in a direction θ varies approximately as $(1+\cos^2\theta)$, whence the fraction of scattered quanta, scattered between θ and $\theta+d\theta$, is $\frac{3}{8}\sin\theta(1+\cos^2\theta)\,d\theta$.

* On Jauncey's theory of the modified radiation, f_2 represents the fraction of the radiation which is modified, and Jauncey derived an expression for it similar to (5).

. The fraction of these which produce recoil tracks is f_2, so that the fraction f_1 of quanta scattered in all directions which give rise to recoil tracks is given by

$$f_1 = \int_0^{\pi} \tfrac{3}{8} \sin\theta(1+\cos^2\theta) \,.\, f_2\, d\theta$$

$$= \int_{\theta_1}^{\theta_2} \tfrac{3}{8} \sin\theta(1+\cos^2\theta) \left\{ \frac{1}{2} + \frac{\psi}{4\mathrm{B}} \sin\frac{\theta}{2} - \frac{\mathrm{V}}{4\psi\mathrm{B}\sin\theta/2} \right\} d\theta$$

$$+ \int_{\theta_2}^{\pi} \tfrac{3}{8} \sin\theta(1+\cos^2\theta)\, d\theta,$$

where θ_1 is given by (6),
and $\theta_2 = \pi$ if $\psi^2 - 2\psi\mathrm{B} - \mathrm{V} < 0$,
and is given by (7) if $\psi^2 - 2\psi\mathrm{B} - \mathrm{V} \geqslant 0$.

This gives on integration

$$f_1 = \left[\frac{3}{4} \left\{ (\delta_2 - \delta_4 - \tfrac{2}{3}\delta_6) + \frac{\psi}{\mathrm{B}} (\tfrac{1}{3}\delta_3 - \tfrac{2}{3}\delta_5 + \tfrac{2}{7}\delta_7) \right.\right.$$

$$\left.\left. - \frac{\mathrm{V}}{\psi\mathrm{B}} (\delta_1 - \tfrac{2}{3}\delta_3 + \tfrac{2}{5}\delta_5) \right\} + g\{1 - \tfrac{3}{2}\beta^2 + \tfrac{3}{2}\beta^4 - \beta^6\} \right], \quad (8)$$

where $g=1$, $\delta_n = \beta^n - \alpha^n$, when $\psi^2 - 2\psi\mathrm{B} - \mathrm{V} \geqslant 0$,
$g=0$, $\delta_n = 1 - \alpha^n$, when $\psi^2 - 2\psi\mathrm{B} - \mathrm{V} < 0$.

This value of f_1 refers to the fraction p of the electrons which have at the instant under consideration orbital energy B^2 and binding energy V.

In the case of electrons which move in elliptic-like orbits the orbital kinetic energy varies continuously between certain limits, and in order to obtain the exact contribution of the whole orbit it is necessary to make an integration. As B enters in a complicated way into f_1 the integration would probably be difficult. The value of f_1 for electrons moving in elliptic-like orbits can, however, be obtained with sufficient accuracy by dividing the range of values of B into finite intervals and then making a summation. For this purpose the intervals defined by $r' = \frac{1}{5}, \frac{2}{5}, \frac{3}{5}, \frac{4}{5}$, and 1 have been chosen, r' being the distance of the electron from the nucleus expressed as a fraction of the maximum values of that distance. The kinetic energy of an electron at a point in its orbit defined by the azimuthal angle γ is proportional to

$$[1 + \epsilon^2 + 2\epsilon\cos\gamma],$$

and is approximately equal to

$$\mathrm{V} \times [1 + \epsilon^2 + 2\epsilon\cos\gamma]/1 - \epsilon^2,$$

ϵ being the eccentricity of the elliptic orbit and V the

binding energy of the electron *. This expression gives the value of B^2 in any interval, so that from (8) the value of f_1 for the electrons concerned can be calculated. In calculating the value of f_1 for circular orbits, the kinetic energy of the electron is taken to be equal to the binding energy, which is approximately true.

The quantity f, whose value we require, is the fraction of the total number of quanta scattered by an atom of the element, which produces recoil electrons that can escape from the atom. The contribution of any class of electrons which constitutes a fraction p of the total number of electrons in the atom is evidently $f_1 \times p$, so that f is given by

$$f = \Sigma f_1 p.$$

The values of f have been calculated for the different elements and different wave-lengths of X-rays used in the various experiments and are given in Table V. Bohr's distribution of the electrons amongst the various orbits has been assumed and the values of V have been obtained from curves given by K. T. Compton and F. L. Mohler †.

Table V.

Gas.	Assumed distributions of electrons in the atoms, and the values of V (in volts).	Wave-length.	f.
Oxygen ...	2K, V=500 : $4L_{21}$, V=50 : $2L_{22}$, V=14	·709 Å	·816
,,	,, ,,	·614	·843
,,	,, ,,	·545	·866
,,	,, ,,	·57	·855
,,	,, ,,	·35	·935
Nitrogen..	2K, V=381 : $4L_{21}$, V=41 : $1L_{22}$, V=11	·614	·850
,,	,, ,,	·545	·876
,,	,, ,,	·57	·863
,,	,, ,,	·35	·940
Argon.....	2K, V=3200 : $4L_{21}$, V=540 : $4L_{22}$, V=410 : $4M_{21}$, V=110 ; $4M_{32}$, V=26	·614	·67
,,	,,	·545	·71
Hydrogen.	1K, V=16.	·614	·971

Summary.

The Wilson cloud method has been used to investigate the short β-ray tracks produced in a gas traversed by X-rays which have been identified with recoil electrons associated with the scattering of the X-rays. In all the experiments

* This expression for the kinetic energy depends on the assumption of the same effective nuclear charge for the calculation of the potential field and the nuclear attracting force.

† Compton and Mohler Bull. Nat. Res. Coun. 9 A, p. 1 (1924).

homogeneous X-rays, produced by reflexion from a crystal, have been used and about 300 stereoscopic pairs of photographs have been examined.

The results which have been obtained refer to the tracks produced in oxygen, nitrogen, and argon by X-rays of wave-lengths ·709 Å*, ·614 Å, and ·545 Å, to those in hydrogen (containing small known percentages of other gases) by X-rays of wave-length ·614 Å, and to those in air by rays of wave-lengths ·57 Å and ·35 Å.

The *distribution* of the short tracks produced in oxygen and nitrogen has been examined and found to be a random one, at least for those short tracks whose origins are separated by more than 1 mm. from the origins of the long tracks.

The ratio N_R/N_P of the number of short tracks to the number of long tracks, according to the theory, should be equal to the ratio of the scattering coefficient to the absorption coefficient multiplied by the fraction f of scattered quanta, which give sufficient energy to the scattering electrons to enable them to leave their parent atoms. The fraction, f, has been calculated on certain assumptions, and an expression obtained for it in terms of the binding energies of the electrons and the wave-length of the radiation. The theoretical values of the ratio N_R/N_P thus obtained are in satisfactory agreement with the observed values of this ratio, which vary from ·029 for argon and radiation of wave-length ·545 Å, to 3·5 for hydrogen (containing a small percentage of oxygen) and rays of wave-length ·614 Å. This consistent agreement over a wide range between the theoretical and observed values strongly supports the quantum theory of scattering and shows that all the scattered radiation obeys that theory. The experiments are being continued with X-rays of shorter wave-length.

In conclusion we should like to express our thanks to Professor C. T. R. Wilson, F.R.S., for his valuable advice on the technique of the method of cloud photography, and to Professor W. L. Bragg, F.R.S., for many helpful suggestions and for his continued interest in the work.

Manchester University,
February 1926.

* Oxygen only.

CX. *The Effect of Axial Restraint on the Stress in a Rotating Disk.* *By* W. G. Green, *B.Sc., A.M.I.N.A.**

§ 1. Introduction.

THE problem on which light is sought is that of a rotating disk carried on a shaft, but a complete solution appears to be out of the question. One effect of the presence of the shaft is to prevent the parts of the disk that are near the axis shifting so far in the direction of the axis as they would if there were no shaft, and it is proposed to trace the consequences of this effect by solving an illustrative problem.

The case treated is that of a disk of outer radius a, and of thickness $2h$, the plane faces being represented by $z = \pm h$. It is assumed that the disk is restrained by concentrated axial tensions P, induced by rotation, at the centres of the outside faces. When such a disk rotates with angular velocity ω, two stress-systems are produced, viz. :

(A) That due to concentrated axial tensions P, in a complete disk at rest.

(B) That due to rotation ω in a complete disk under no superficial tractions.

For the first, it is essential to regard the radius of the disk as infinite, but the results obtained, however, show that the error due to this assumption is small. For the second, Chree's solution † will be taken. By compounding these two stress-systems, the total stress-components and displacements can be determined. For the determination of P in terms of ω, it will be assumed that the axial displacement $w=0$ when $z = \pm h$, $r = r_1$, where r_1 may be taken to represent the radius of the shaft.

Before developing the analysis on the lines of the résumé given above, it is necessary to mention the stresses arising from a concentrated force acting at a point on the plane boundary of an elastic solid.

* Communicated by Prof. A. E. H. Love.

† A. E. H. Love, 'Mathematical Theory of Elasticity,' 3rd edn. § 102, Case (*b*).

§ 2. Pressure at a Point on a Plane Boundary *.

Taking the origin to be the point at which the load is applied, the plane $z=0$ to be the bounding surface of the body, and the positive direction of the axis of z to be that which passes into the interior of the body, then, expressing the results in cylindrical coordinates, the tractions across a plane parallel to the plane boundary are

$$\widehat{zz} = \frac{3P}{2\pi} \cdot \frac{z^3}{(z^2+r^2)^{5/2}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\widehat{zr} = \frac{3P}{2\pi} \cdot \frac{z^2 r}{(z^2+r^2)^{5/2}}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P is the applied load, and is positive for tension,

$\widehat{zz}$ is the direct stress parallel to the direction of P,

$\widehat{zr}$ is the shear stress in planes passing through the line of action of P.

It will be necessary to express these tractions in terms of definite integrals involving Bessel's Functions, of order zero and unity respectively. The required expressions can be deduced easily from the well-known result

$$\int_0^\infty e^{-kz} J_0(kr)\, dk = (r^2+z^2)^{-\frac{1}{2}} \quad . \quad . \quad . \quad (3)$$

by differentiation, with respect to z and r, under the sign of integration. Hence it follows that

$$\widehat{zz} = \frac{P}{2\pi} \int_0^\infty k(1+kz)\, e^{-kz} J_0(kr)\, dk, \quad . \quad . \quad . \quad (4)$$

$$\widehat{zr} = \frac{P}{2\pi} \int_0^\infty k^2 z\, e^{-kz} J_1(kr)\, . dk. \quad . \quad . \quad . \quad . \quad (5)$$

Using these results, the stress-system due to concentrated axial tensions P, in a complete disk at rest, can be developed.

§ 3. The Stress-System (A), due to concentrated axial tensions P, in a complete disk at rest.

(a) It is convenient to subdivide this system into three component systems as follows :—

* Love, *op. cit.* § 135.

I. That due to an axial tension P, acting at the surface of an infinite solid bounded by the plane $z=-h$, and lying on the side $z>-h$ of this plane.

Here equations (4) and (5) become

$$\widehat{zz}_1 = \frac{P}{2\pi}\int_0^\infty k\{1+k(h+z)\}\,e^{-k(h+z)}\,J_0(kr)\,dk, \quad . \quad (6)$$

$$\widehat{zr}_1 = \frac{P}{2\pi}\int_0^\infty k^2(h+z)\,e^{-k(h+z)}\,J_1(kr)\,dk, \quad . \quad . \quad . \quad (7)$$

giving stress-components at $z=h$

$$\widehat{zz}_1 = \frac{P}{2\pi}\int_0^\infty k(1+2hk)\,e^{-2hk}\,J_0(kr)\,dk, \quad . \quad . \quad (8)$$

$$\widehat{zr}_1 = \frac{P}{2\pi}\int_0^\infty 2hk^2\,e^{-2hk}\,J_1(kr)\,dk. \quad . \quad (9)$$

II. That due to an axial tension P, acting at the surface of an infinite solid bounded by the plane $z=h$, and lying on the side $z<h$ of this plane. In this case equations (4) and (5) become

$$\widehat{zz}_2 = \frac{P}{2\pi}\int_0^\infty k\{1+k(h-z)\}\,e^{-k(h-z)}\,J_0(kr)\,dk, \quad . \quad (10)$$

$$\widehat{zr}_2 = -\frac{P}{2\pi}\int_0^\infty k^2(h-z)\,e^{-k(h-z)}\,J_1(kr)\,dk, \quad . \quad . \quad . \quad (11)$$

giving stress-components at $z=-h$

$$\widehat{zz}_2 = \frac{P}{2\pi}\int_0^\infty k(1+2hk)\,e^{-2hk}\,J_0(kr)\,dk, \quad . \quad . \quad (12)$$

$$\widehat{zr}_2 = -\frac{P}{2\pi}\int_0^\infty 2hk^2\,e^{-2hk}\,J_1(kr)\,dk. \quad . \quad . \quad . \quad . \quad (13)$$

III. The system in the infinite slab contained between the planes $z=\pm h$, these planes being subject to tractions obtained by reversing the components $\widehat{zz}$ and $\widehat{zr}$ at $z=h$ in I, and at $z=-h$ in II.

By compounding the systems I, II, and III, the stress-components in the complete disk at rest, due to the concentrated axial tensions P, can be determined.

(b) *Determination of the Stress-Components.*

For symmetrical strain in a solid of revolution *, the results may be expressed in terms of a function χ which

* Love, *op. cit.* § 188.

satisfies the differential equation $\nabla^4\chi=0$, where

$$\nabla^2\chi \equiv \left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{\partial^2}{\partial z^2}\right) \equiv \left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}+\frac{\partial^2}{\partial z^2}\right).$$

The stress-components are then given by

$$\left.\begin{aligned} \widehat{rr} &= \frac{\partial}{\partial z}\left[\sigma\,.\,\nabla^2\chi-\frac{\partial^2\chi}{\partial r^2}\right], \\ \widehat{\theta\theta} &= \frac{\partial}{\partial z}\left[\sigma\,.\,\nabla^2\chi-\frac{1}{r}\frac{\partial\chi}{\partial r}\right], \\ \widehat{zz} &= \frac{\partial}{\partial z}\left[(2-\sigma)\nabla^2\chi-\frac{\partial^2\chi}{\partial z^2}\right], \end{aligned}\right\} \quad . \quad . \quad . \quad (14)$$

$$\widehat{zr} = \frac{\partial}{\partial r}\left[(1-\sigma)\,.\,\nabla^2\chi-\frac{\partial^2\chi}{\partial z^2}\right], \quad . \quad . \quad . \quad (15)$$

and the displacements by

$$\left.\begin{aligned} u &= -\frac{1+\sigma}{\mathrm{E}}\,.\,\frac{\partial^2\chi}{\partial r\,\partial z}, \\ w &= \frac{1+\sigma}{\mathrm{E}}\,.\left[(1-2\sigma)\nabla^2\chi+\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial\chi}{\partial r}\right]. \end{aligned}\right\} \quad . \quad (16)$$

A solution for χ may be written

$$\chi = \Sigma\,\mathrm{J}_0(kr)\left[\left(\mathrm{C}+\frac{z}{2k}\,.\,\mathrm{A}\right)e^{kz}+\left(\mathrm{D}-\frac{z}{2k}\,.\,\mathrm{B}\right)e^{-kz}\right],$$

where

$$\nabla^2\chi = \Sigma\,\mathrm{J}_0(kr)\,[\mathrm{A}e^{kz}+\mathrm{B}e^{-kz}],$$

the summation being for any number of values of k; A, B, C, and D being arbitrary constants.

In the stress-system due to pressure at a point on a plane boundary, § 2, A and C are both zero, and it can be readily shown that the value

$$\chi = \frac{\mathrm{P}}{2\pi}\int_0^\infty \frac{1}{k^2}[\{2\sigma+kz\}\,e^{-kz}\,\mathrm{J}_0(kr)-\{2\sigma+kz(1-2\sigma)\}]\,dk, \quad . \quad . \quad . \quad (17)$$

together with equations (14) and (15), will give correctly the expressions for $\widehat{zz}$ and $\widehat{zr}$, equations (4) and (5).

Again, in the stress-system III, due to the reversed tractions, $\mathrm{C}=-\mathrm{D}$, $\mathrm{A}=-\mathrm{B}$, giving a symmetrical solution.

Using these results it is now possible to write down the functions χ_1, χ_2, χ_3, representing the systems I, II, and III, respectively, and rearranging the constants in the latter case,

we have

$$\chi_1 = \frac{P}{2\pi}\int_0^\infty \frac{1}{k^2}\left[\{2\sigma + k(h+z)\}\, e^{-k(h+z)}\, J_0(kr) - \{2\sigma + (1-2\sigma)k(h+z)\}\right] dk, \quad (18)$$

$$\chi_2 = -\frac{P}{2\pi}\int_0^\infty \frac{1}{k^2}\left[\{2\sigma + k(h-z)\}\, e^{-k(h-z)}\, J_0(kr) - \{2\sigma + (1-2\sigma)k(h-z)\}\right] dk, \quad (19)$$

$$\chi_3 = \frac{P}{\pi}\int_0^\infty \frac{1}{k^2}\left[(\alpha \sinh kz - \beta\, kz \cosh kz)\, J_0(kr) - (\alpha-\beta)\, kz\right] dk. \quad (20)$$

The linear functions of z, included in the above expressions, secure that the integral is convergent in each case.

(c) *Evaluation of the Stress-Components* I.

From equation (18) it follows that

$$\left.\begin{aligned} \frac{1}{r}\frac{\partial \chi_1}{\partial r} &= -\frac{P}{2\pi}\int_0^\infty \{2\sigma + k(h+z)\}\, e^{-k(h+z)}\frac{J_1(kr)}{(kr)}\, dk, \\ \frac{1}{r}\frac{\partial}{\partial r}\, r\, \frac{\partial \chi_1}{\partial r} &= -\frac{P}{2\pi}\int_0^\infty \{2\sigma + k(h+z)\}\, e^{-k(h+z)}\, J_0(kr)\, dk, \\ \frac{\partial^2 \chi_1}{\partial z^2} &= -\frac{P}{2\pi}\int_0^\infty \{2(1-\sigma) - k(h+z)\} e^{-k(h+z)}\, J_0(kr)\, dk, \\ \nabla^2 \chi_1 &= -\frac{P}{\pi}\int_0^\infty e^{-k(h+z)}\, J_0(kr)\, dk. \end{aligned}\right\} \quad (21)$$

Substituting in equations (14), and using the relation

$$\frac{\partial^2 \chi}{\partial r^2} = \frac{1}{r}\frac{\partial}{\partial r}\, r\, \frac{\partial \chi}{\partial r} - \frac{1}{r}\cdot\frac{\partial \chi}{\partial r},$$

the stress-components may be written

$$\left.\begin{aligned} \widehat{rr}_1 &= \frac{P}{2\pi}\int_0^\infty e^{-k(h+z)}\left[2\sigma\cdot\frac{J_1(kr)}{kr} + \{1-k(h+z)\}\left\{J_0(kr) - \frac{J_1(kr)}{kr}\right\}\right] k\, dk, \\ \widehat{\theta\theta}_1 &= \frac{P}{2\pi}\int_0^\infty e^{-k(h+z)}\left[\{1-k(h+z)\}\frac{J_1(kr)}{kr} + 2\sigma\left\{J_0(kr) - \frac{J_1(kr)}{kr}\right\}\right] k\, dk, \\ \widehat{zz}_1 &= \frac{P}{2\pi}\int_0^\infty e^{-k(h+z)}\, \{1 + k(h+z)\, J_0(kr)\, k\, dk. \end{aligned}\right\} \quad (22)$$

These components may be evaluated graphically, in the manner used for the stress-system III, to be described later. The component $\widehat{zz}_1$ is, however, given directly by equation (1), and may be written

$$\widehat{zz}_1 = \frac{3P}{2\pi} \cdot \frac{(h+z)^3}{\{(h+z)^2+r^2\}^{5/2}}. \quad . \quad . \quad . \quad (23)$$

The components $\widehat{rr}_1$ and $\theta\theta_1$ can also be calculated directly by using Polar Coordinates *. See Appendix.

A similar set of expressions can be developed for the stress-system II, but the results are easily obtained from those already given.

(d) *Evaluation of the Stress-Components* III.

Proceeding as before, equation (20) gives

$$\left.\begin{aligned}
\frac{1}{r}\frac{\partial\chi_3}{\partial r} &= -\frac{P}{\pi}\int_0^\infty \{\alpha \sinh kz - \beta kz \cosh kz\}\frac{J_1(kr)}{kr}\,dk,\\
\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial\chi_3}{\partial r} &= -\frac{P}{\pi}\int_0^\infty \{\alpha \sinh kz - \beta kz \cosh kz\}\,J_0(kr)\,dk,\\
\frac{\partial^2\chi_3}{\partial z^2} &= \frac{P}{\pi}\int_0^\infty \{(\alpha-2\beta)\sinh kz \\
&\qquad - \beta kz \cosh kz\}\,J_0(kr)\,dk,\\
\nabla^2\chi_3 &= -\frac{P}{\pi}\int_0^\infty 2\beta \sinh kz\, J_0(kr)\,dk.
\end{aligned}\right\} \quad . \quad . \quad . \quad (24)$$

So that substituting in equations (14) and (15), as before, the stress-components become

$$\left.\begin{aligned}
\widehat{rr}_3 &= -\frac{P}{\pi}\int_0^\infty \left[2\beta\sigma \cosh kz\,.\,J_0(kr) - \{\quad J_0(kr) - \frac{J_1(kr)}{kr}\right\} \\
&\qquad \times \{(\alpha-\beta)\cosh kz - \beta kz \sinh kz\}\Big]\,k\,dk,\\
\widehat{\theta\theta}_3 &= -\frac{P}{\pi}\int_0^\infty \left[2\beta\sigma \cosh kz\,.\,J_0(kr) - \frac{J_1(kr)}{kr}\right. \\
&\qquad \times \{(\alpha-\beta)\cosh kz - \beta kz \sinh kz\}\Big]\,k\,dk,\\
\widehat{zz}_3 &= -\frac{P}{\pi}\int_0^\infty \Big[\{\alpha+\beta(1-2\sigma)\}\cosh kz - \beta kz \sinh kz\Big] \\
&\qquad \times J_0(kr)\,k\,dk,
\end{aligned}\right\} \quad . \quad . \quad . \quad (25)$$

* Love, *op. cit.* § 142, Case (i). Putting $\alpha = \frac{\pi}{2}$, we obtain the solution for pressure at a point on a plane boundary, expressed in Polar Co-ordinates.

$$\widehat{zr}_3 = -\frac{P}{\pi}\int_0^\infty \left[\beta kz\cosh kz - (\alpha - 2\beta\sigma)\sinh kz\right] J_1(kr)\,k\,dk. \quad . \quad . \quad . \quad (26)$$

Now the condition for the determination of the constants α and β is obtained by reversing the tractions I at $z=h$, or the tractions II at $z=-h$. Hence, at $z=h$, we must have

$$\widehat{zr}_3 = -\widehat{zr}_1,$$

$$\widehat{zz}_3 = -\widehat{zz}_1,$$

so that, combining equations (8) and (9) with the expressions for zz_3, and $\widehat{zr}_3$, when $z=h$, given by equations (25) and (26), we have, for a particular value of k,

$$\{\alpha+\beta(1-2\sigma)\}\cosh kh - \beta\, kh\sinh kh = \frac{1+2hk}{2}\cdot e^{-2hk},$$

$$\beta\, kh\,.\cosh kh - (\alpha - 2\beta\sigma)\sinh kh = hk\,.\,e^{-2hk}.$$

Solving these equations for α and β, the latter become

$$\alpha = e^{-2hk}\cdot\frac{\left[\begin{array}{l}\{2\sigma(1+2hk)+2h^2k^2\}\sinh kh \\ +\{hk(1+2hk)-2hk(1-2\sigma)\}\cosh kh\end{array}\right]}{2hk+\sinh 2hk}, \quad . \quad . \quad . \quad (27)$$

$$\beta = e^{-2hk}\cdot\frac{[(1+2hk)\sinh kh + 2hk\cosh kh]}{2hk+\sinh 2hk}. \quad . \quad . \quad . \quad (28)$$

These expressions show α and β to be functions of hk, and, assuming Poisson's Ratio $\sigma = \cdot 3$, calculated values of these constants are given in Table I.

TABLE I.

hk.	α.	β.
0	·200	·750
·25	·262	·531
·50	·265	·368
1·0	·1891	·1592
1·5	·0995	·0595
2·0	·0418	·0194
3·0	·00489	·001555
4·0	·000428	·0001036

The stress-components, given by equations (25), can now be evaluated graphically. The integrals, in every case, may be expressed as functions of hk, by taking points whose co-ordinates r, z, are multiples, or sub-multiples, of h. Using the tabulated values of α and β, and the appropriate values of Bessel's Functions *, the subject of integration can be calculated for definite values of hk, and a curve drawn showing the variation of this function with hk. The area under the curve having been determined, by means of a planimeter, or otherwise, we can then write

$$\text{Stress-Component} = \delta_3 \cdot \frac{P}{\pi h^2},$$

where δ_3 is a numerical constant, representing the stress components in system III. Taking $\sigma = \cdot 3$, as before, values of δ_3 are given in Table II.

TABLE II.

	Plane $z = 0$.			Plane $z = \frac{h}{2}$.			Plane $z = h$.		
	$\widehat{rr}_3$.	$\widehat{\theta\theta}_3$.	$\widehat{zz}_3$.	$\widehat{rr}_3$.	$\widehat{\theta\theta}_3$.	$\widehat{zz}_3$.	$\widehat{rr}_3$.	$\widehat{\theta\theta}_3$.	$\widehat{zz}_3$.
$r = 0$	−·133	−·133	−·417	−·186	−·186	−·430	−·474	−·474	−·375
$r = \frac{h}{2}$	−·133	−·124	−·368	−·172	−·176	−·372	−·372	−·405	−·322
$r = h$	−·126	−·102	−·259	−·148	−·137	−·251	−·206	−·276	−·215
$r = 2h$	−·084	−·062	−·075	−·073	−·070	−·070	−·017	−·088	−·066
$r = 3h$	−·036	−·034	−·011	−·026	−·039	−·013	−·000	−·040	−·020

(e) *Calculated Values of the Stress-Components in the complete disk at rest.*

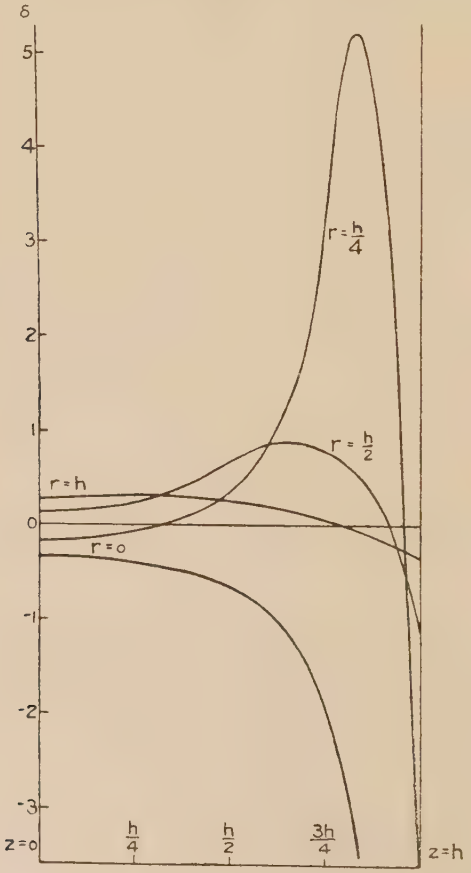
The stress-components I and II, for points corresponding to those taken in system III, have been calculated, using Polar Coordinates for the $\widehat{rr}$, $\widehat{\theta\theta}$ values, as already indicated. Reducing them to the same form as before, these components

* Jahnke and Emde, 'Funktionentafeln mit Formeln und Kurven,' Teubner, 1909.

TABLE III.

	Plane $z = 0$.			Plane $z = \frac{h}{2}$.			Plane $z = h$.		
	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.
$r = 0$	−·333	−·333	2·583	−·630	−·630	6·237	—	—	—
$r = \frac{h}{2}$	·128	−·240	1·348	·671	−·259	1·201	−1·176	·373	0
$r = h$	·287	−·126	·271	·260	−·116	·122	−·373	−·089	0
$r = 2h$	·076	−·042	−·021	·041	−·046	−·013	−·015	−·041	0
$r = 3h$	·019	−·016	−·002	·017	−·020	−·000	·015	−·019	0

Fig. 1.—δ Values for Component *rr*.

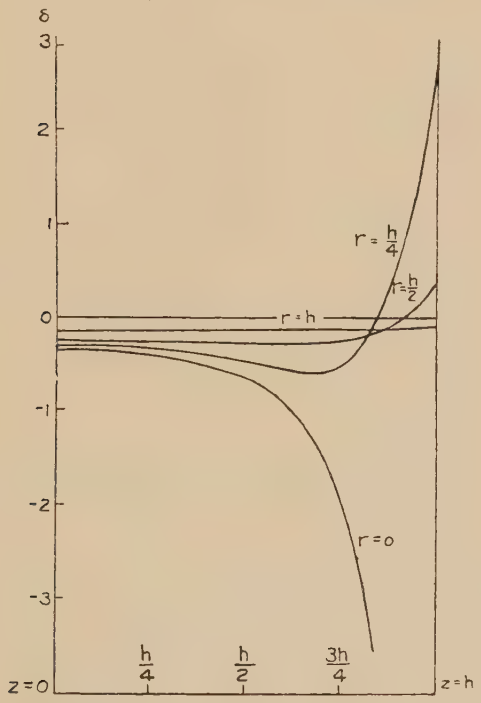


may be represented by numerical constants δ_1 and δ_2. Compounding the three systems, and writing

$$\delta = \delta_1 + \delta_2 + \delta_3,$$

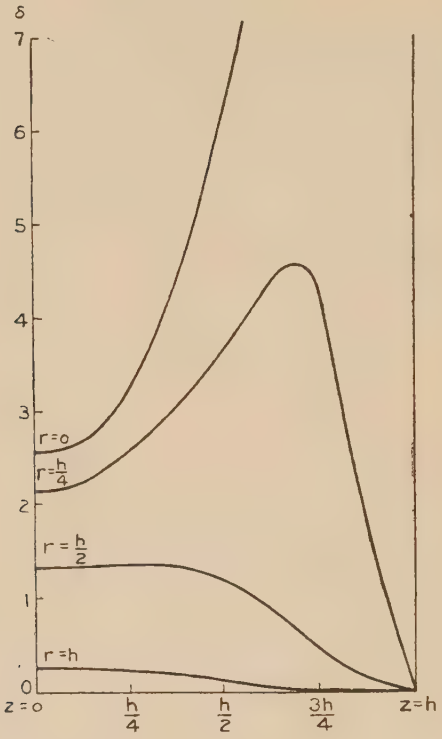
values of δ, representing the stress-components in the complete disk at rest, are given in Table III., and in figs. 1, 2, and 3.

Fig. 2.—δ Values for Component $\widehat{\theta\theta}$.



It should be remembered that the expressions giving the stresses arising from "pressure at a point on a plane boundary" are true for all points not too near the origin, when the pressure is applied at the origin. Hence the above analysis is true for all points not too near the centres of the outside faces of the disk.

Fig. 3.—δ Values for Component $\widehat{zz}$.



§ 4. The Stress-System (B) due to Rotation only.

The results of the solution due to Chree * are summarized below for convenience. The stress-components are given by

$$\left.\begin{aligned} \widehat{rr} &= \frac{\rho\omega^2}{8}(3+\sigma)(a^2-r^2) + \frac{\rho\omega^2}{6}\cdot\sigma\cdot\frac{1+\sigma}{1-\sigma}(h^2-3z^2), \\ \widehat{\theta\theta} &= \frac{\rho\omega^2}{8}\{(3+\sigma)a^2-(1+3\sigma)r^2\} + \frac{\rho\omega^2}{6}\sigma\cdot\frac{1+\sigma}{1-\sigma}(h^2-3z^2), \\ \widehat{zz} &= \widehat{zr} = 0, \end{aligned}\right\} \quad \ldots \quad (29)$$

* Love, *op. cit.* § 102, Case (*b*).

and the displacements by

$$\left.\begin{aligned} u = {} & \frac{\rho\omega^2 r}{8\mathrm{E}}(1-\sigma)\{(3+\sigma)a^2-(1+\sigma)r^2\} \\ & \qquad + \frac{\rho\omega^2 . r}{6\mathrm{E}}\sigma(1+\sigma)(h^2-3z^2), \\ w = {} & -\frac{\rho\omega^2 z}{4\mathrm{E}} . \sigma\{(3+\sigma)a^2-2(1+\sigma)r^2\} \\ & \qquad - \frac{\rho\omega^2 z}{3\mathrm{E}}\sigma^2 . \frac{1+\sigma}{1-\sigma}(h^2-z^2). \end{aligned}\right\} \quad . \ . \ . \quad (30)$$

§ 5. Determination of the Axial Tensions.

(a) *Axial displacements in the Stress-System* A.

Equation (16) gives the axial displacement w in terms of the function χ.

Now

$$\left.\begin{aligned} \nabla^2\chi_1 &= -\frac{\mathrm{P}}{\pi}\int_0^\infty e^{-k(h+z)}\,\mathrm{J}_0(kr)\,dk, \\ \nabla^2\chi_2 &= \frac{\mathrm{P}}{\pi}\int_0^\infty e^{-k(h-z)}\,\mathrm{J}_0(kr)\,dk, \\ \nabla^2\chi_3 &= -\frac{\mathrm{P}}{\pi}\int_0^\infty 2\beta\sinh kz\,\mathrm{J}_0(kr)\,dk, \end{aligned}\right\} \quad . \ . \quad (31)$$

and

$$\left.\begin{aligned} \frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial\chi_1}{\partial r} &= -\frac{\mathrm{P}}{2\pi}\int_0^\infty e^{-k(h+z)}\,\mathrm{J}_0(kr)\,\{2\sigma+k(h+z)\}\,dk, \\ \frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial\chi_2}{\partial r} &= \frac{\mathrm{P}}{2\pi}\int_0^\infty e^{-k(h-z)}\,\mathrm{J}_0(kr)\,\{2\sigma+k(h-z)\}\,dk, \\ \frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial\chi_3}{\partial r} &= -\frac{\mathrm{P}}{\pi}\int_0^\infty \{\alpha\sinh kz - \beta kz\cosh kz\}\,\mathrm{J}_0(kr)\,dk. \end{aligned}\right\}$$

. . . (32)

Substituting in equation (16), the displacements are given by

$$\left.\begin{aligned} w_1 &= -\frac{\mathrm{P}}{2\pi}\cdot\frac{1+\sigma}{\mathrm{E}}\int_0^\infty e^{-k(h+z)}\,\mathrm{J}_0(kr)\,\{2(1-\sigma)+k(h+z)\}\,dk, \\ w_2 &= \frac{\mathrm{P}}{2\pi}\cdot\frac{1+\sigma}{\mathrm{E}}\int_0^\infty e^{-k(h-z)}\,\mathrm{J}_0(kr)\,\{2(1-\sigma)+k(h-z)\}\,dk, \\ w_3 &= -\frac{\mathrm{P}}{\pi}\cdot\frac{1+\sigma}{\mathrm{E}}\int_0^\infty [\{\alpha+2\beta(1-2\sigma)\}\sinh kz-\beta kz\cosh kz] \\ & \qquad \mathrm{J}_0(kr)\,dk. \end{aligned}\right\}$$

. . . (33)

Putting $z=h$, $r=r_1$, these become

$$\left.\begin{aligned} w_1 &= -\frac{P}{\pi h}\cdot\frac{1+\sigma}{E}\int_0^\infty e^{-2kh}\,J_0(kr_1)\,\{(1-\sigma)+kh\}\,d(kh),\\ w_2 &= \frac{P}{\pi r_1}\cdot\frac{1-\sigma^2}{E},\\ w_3 &= -\frac{P}{\pi h}\cdot\frac{1+\sigma}{E}\int_0^\infty [\{\varepsilon+2\beta(1-2\sigma)\}\sinh kh-\beta kh\cosh kh]\\ &\qquad\times J_0(kr_1)\,d(kh). \end{aligned}\right\} \quad . \quad . \quad . \quad (34)$$

Expressing these displacements in the form

$$w_1=\gamma_1\cdot\frac{P}{\pi hE}\ \text{etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where $\gamma=\gamma_1+\gamma_2+\gamma_3$,

and integrating w_1 and w_3 graphically, numerical values of γ are given in Table IV.

TABLE IV.

	γ_1.	γ_2.	γ_3.	γ.
$r_1=\frac{h}{4}$	−·774	3·640	−·272	2·594
$r_1=\frac{h}{2}$	−·754	1·820	−·243	·823
$r_1=\frac{3h}{4}$	−·712	1·213	−·203	·298
$r_1=h$	−·646	·910	−·156	·108

(b) *Determination of P.*

The condition of restraint assumed is that the resultant axial displacement vanishes at $z=\pm h$, $r=r_1$. Due to pure rotation, the axial displacement at $z=h$, $r=r_1$ is given by equation (30), and is

$$w=-\frac{\rho\omega^2 h}{4E}\sigma\{(3+\sigma)a^2-2(1+\sigma)r_1^2\}. \quad . \quad . \quad (36)$$

The displacements given by equations (35) and (36) must

therefore neutralize each other, hence

$$\frac{P}{\pi h^2} = \rho w^2 a^2 \frac{\sigma}{4\gamma}\left\{(3+\sigma)-2(1+\sigma)\frac{r_1^2}{a^2}\right\}, \quad . \quad (37)$$

and if $\sigma = \cdot 3$ this gives

$$\frac{P}{\pi h^2} = \frac{\rho\omega^2 a^2}{\gamma}\left\{\cdot 2475 - \cdot 195\frac{r_1^2}{a^2}\right\}. \quad . \quad . \quad (38)$$

§ 6. Total Stress-Components when Rotating under Restraint.

These are obtained by compounding the stress-systems A and B. In the former we can now write

$$\text{Stress-Component} = \delta\frac{P}{\pi h^2} = \rho\omega^2 a^2 . \frac{\delta}{\gamma}\left\{\cdot 2475 - \cdot 195\frac{r_1^2}{a^2}\right\}. \quad . \quad . \quad . \quad (39)$$

Values of δ are given by Table III. and the accompanying diagrams. For a given value of r_1 the appropriate value of γ can be determined from the results given in Table IV. Thus, equation (39) gives the stress-component at any point in the system A, for any assumed condition of restraint.

For the stress-system B, equations (29) determine the stress-components at any point.

To illustrate the effect of restraint, consider the case when $r_1 = \frac{h}{2}$. The value of γ given by Table IV. is ·823, and so equation (39) becomes

$$\text{Stress-Component} = \rho\omega^2 a^2 . \delta\left\{\cdot 301 - \cdot 0593\frac{h^2}{a^2}\right\}. \quad (40)$$

Further, considering the stresses at the point $r = \frac{h}{2}$, $z = \frac{h}{2}$, and substituting the appropriate values of δ, given in Table III., we have, in the stress-system A,

$$\left.\begin{aligned} \widehat{rr} &= \quad \rho\omega^2 a^2\left\{\cdot 202 - \cdot 0398\frac{h^2}{a^2}\right\}, \\ \widehat{\theta\theta} &= -\rho\omega^2 a^2\left\{\cdot 078 - \cdot 0154\frac{h^2}{a^2}\right\}, \\ \widehat{zz} &= \quad \rho\omega^2 a^2\left\{\cdot 362 - \cdot 0713\frac{h^2}{a^2}\right\}, \end{aligned}\right\} \quad . \quad . \quad . \quad (41)$$

For the stress-system B, when $r = \frac{h}{2}$, $z = \frac{h}{2}$, equations (29) give

$$\left.\begin{aligned} \widehat{rr} &= \rho\omega^2 a^2 \left\{ \cdot 4125 - \cdot 0799 \frac{h^2}{a^2} \right\}, \\ \widehat{\theta\theta} &= \rho\omega^2 a^2 \left\{ \cdot 4125 - \cdot 0362 \frac{h^2}{a^2} \right\}, \\ \widehat{zz} &= 0. \end{aligned}\right\} \quad . \quad . \quad (42)$$

The total stress-components, at $r = \frac{h}{2}$, $z = \frac{h}{2}$, are therefore

$$\left.\begin{aligned} \widehat{rr} &= \rho\omega^2 a^2 \left\{ \cdot 6145 - \cdot 1197 \frac{h^2}{a^2} \right\}, \\ \widehat{\theta\theta} &= \rho\omega^2 a^2 \left\{ \cdot 3345 - \cdot 0208 \frac{h^2}{a^2} \right\}, \\ \widehat{zz} &= \rho\omega^2 a^2 \left\{ \cdot 362 \ - \cdot 0713 \frac{h^2}{a^2} \right\}. \end{aligned}\right\} \quad . \quad . \quad (43)$$

Similar expressions may be obtained for all points.

§ 7. The Effect of the Radius of the Shaft.

The greater the diameter of the shaft, the more effective it becomes in restricting the axial movement of parts of the disk that are near the axis. This effect is shown clearly by the variation in the value of γ for different values of r_1 given in Table IV. The theory is limited, however, by the fact that the effect of the shaft is not concentrated, and the result of this distribution is that, for values of r less than r_1, the stress-components tend to definite finite limits on approaching the planes $z = \pm h$, instead of tending to infinite and zero values as shown in figs. 1, 2, and 3. It should be borne in mind that the assumption of concentrated axial tensions is merely a means of effecting restraint, and in a disk carried on a shaft of radius r_1, the theory indicates the stress distribution for values of r equal to or greater than r_1. A more complete application of the foregoing analysis to practical conditions, although of great importance, should hardly, perhaps, be considered here, and might with advantage be dealt with subsequently.

Appendix.

Pressure at a point on a plane boundary, referred to Polar Coordinates *.

Referred to Polar Coordinates, the stress-components are expressed by the equations

$$\left.\begin{aligned}
\widehat{rr} &= \frac{P}{2\pi r^2}(1-2\sigma)\left[\frac{2(2-\sigma)}{(1-2\sigma)}\cos\theta - 1\right], \\
\widehat{\theta\theta} &= -\frac{P}{2\pi r^2}(1-2\sigma)\cdot\frac{\cos^2\theta}{1+\cos\theta}, \\
\widehat{\phi\phi} &= \frac{P}{2\pi r^2}(1-2\sigma)\left[\frac{1}{1+\cos\theta} - \cos\theta\right],
\end{aligned}\right\} \quad . \quad \text{(i.)}$$

$$r\theta = -\frac{P}{2\pi r^2}(1-2\sigma)\frac{\sin\theta\,.\,\cos\theta}{1+\cos\theta}, \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

where, as in § 2, the origin is the point at which the load is applied, the axis being the line $\theta = 0$, and the positive direction of r is that which goes into the interior of the body.

The component $\widehat{\theta\theta}$, expressed by Cylindrical Coordinates, is the component $\widehat{\phi\phi}$ of equations (i.), and the component $\widehat{rr}$, of the preceding analysis, may be expressed in terms of Polar Coordinates by writing

$$\text{Radial Component} = \widehat{rr}\sin^2\theta + \widehat{\theta\theta}\cos^2\theta + \widehat{r\theta}\sin 2\theta\,\dagger, \quad \text{(iii.)}$$

where $\widehat{rr}$, $\widehat{\theta\theta}$, $\widehat{r\theta}$ are given by equations (i.) and (ii.).

In conclusion, the writer wishes to record his indebtedness to Professor Love for the helpful suggestions and advice he has received relative to the solution of this problem.

R.N. Engineering College,
Keyham, Devonport,
February 1926.

* See footnote, p. 1241.
† Love, *op. cit.* § 49.

CXI. *Determination of Surface-Tension by the Method of Ripples.* *By* P. N. Ghosh, D. Banerji, *and* S. K. Datta *.

[Plate XXI.]

1. *Introduction.*

LORD RAYLEIGH † developed the method of measuring the surface-tension of water by causing a thin blade of glass attached to one of the prongs of a tuning-fork of known frequency to excite ripples on its surface. These ripples were then viewed stroboscopically through a slit attached to the prongs of another fork of submultiple frequency. For keeping the amplitude within a low limit and at the same time to observe the ripples distinctly, the well-known Foucault arrangement was used to illuminate the surface of water on which the ripples are excited. Observing such stationary ripples in the direction of their propagation, they appear as alternate dark and bright bands, the distance between two consecutive dark or bright bands giving the wave-length.

The theory of such travelling ripples was worked on a hydrodynamical basis by Lord Kelvin ‡, and is expressed by the formula:—

$$\sigma = \frac{\lambda^3 n^2 \rho}{2\pi} - \frac{g\lambda^2 \rho}{4\pi^2},$$

where

σ = surface-tension,
λ = wave-length,
n = frequency of the fork,
ρ = density of the liquid.

The ripple method has since then been worked by Dorsey §, Grunmach ‖, Kalähne ¶, Brummer **, Kolowrat-Tscherinsky †† in determining surface-tension of water.

Owing to the difficulty of the stroboscopic arrangement, Grunmach and others produced stationary wave-patterns by the superposition of two systems of waves produced by fine styles attached to the two prongs of the fork.

* Communicated by the Authors.

† Lord Rayleigh, Scientific Papers, vol. iii. pp. 383–396.

‡ Lord Kelvin, Math. and Physical Papers, vol. iv. & Phil. Mag. (4), xlii. p. 368 (1871).

§ Dorsey, Phil. Mag. (5), xliv. p. 369 (1897).

‖ Grunmach, *Ann. der Physik*, ix. p. 1283 (1902).

¶ Kalähne, *Ann. der Physik*, vii. p. 462 (1902).

** Brummer, Rostock Dissert., 1903.

†† Kolwrat-Tscherinsky, *Journal d. russ Phys. Chem. Gess.* xxxvi. p. 265 (1904).

The main difficulties in the Rayleigh arrangement are the following :—

(1) The stroboscopic arrangement was not perfect, as slight disagreement in frequency relations between the exciting and the viewing fork affects the stationary character of the ripples, producing a variation in the position and width of the bright and dark bands.

(2) The estimation of λ by measuring appliances other than by an accurate micrometer is liable to lead to errors, which magnify themselves in the final computation of σ.

(3) The frequency of the exciting fork should be determined accurately while it is exciting the ripples. The frequency of the fork is modified owing to the contact of the liquid-surface, and as the square of the frequency occurs in the calculation of the surface-tension, a slight error in the estimation of this factor modifies the result considerably.

As to the methods of interference used by other workers, it is to be pointed out that the formation of true capillary ripples depends on the smallness of the amplitude of excitation. Unless, however, the intensity of the two sets of waves attains an appreciable value, the interference pattern is hardly perceptible, leading to uncertainty in the measurement of wave-length.

Some preliminary experiments to find out the effect of amplitude of the ripples and the value of the surface-tension showed that the increase in amplitude led to higher values.

The values of surface-tension as determined by several investigators using different methods are found to vary considerably among themselves, as is shown by the following graph (fig. 1). The curves *a*, *b*, *c*, *d* show the results as found by them.

It is noticed in these curves that the lowest values are given by the capillary-tube method, and the highest are those from the adhesion ring. Lord Rayleigh's values are intermediate between them.

The present work has been undertaken to find out whether the ripple method carefully conducted would lead to results in conformity with other methods.

2. *The New Arrangement of the Ripple Method.*

(1) The present authors adopted the method of ripples, and in a note to 'Nature' * described a device in which the stroboscopic effect was perfect inasmuch as a second fork was not necessary.

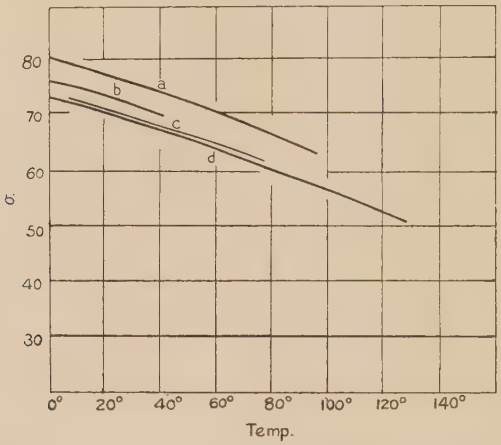
* 'Nature,' xiv. (1925).

(2) Photographic records of the ripple forms were taken.

(3) The frequency of the fork was determined with the help of a standardized seconds pendulum and a chronographic record.

(4) The amplitude of the vibrating plate was kept within low limits.

Fig. 1.

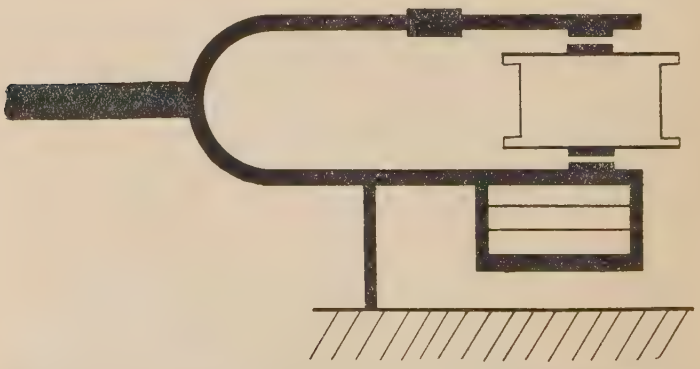


a = Adhesion ring (Weinberg). *c* = Capillary tube (Weinstein).
b = Hanging drops (Sentis). *d* = Capillary tube (Ramsay & Shields).

The method is described in detail as follows :—

To the lower prong of electrically-maintained tuning-fork frequency (about 100 d.v.), rigidly fixed to a heavy base, is

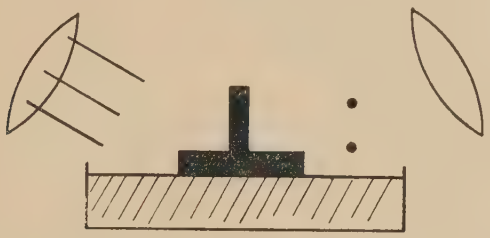
Fig. 2.



attached a rectangular framework of aluminium having two fine steel wires running horizontally along the length of the framework (fig. 2).

A horizontal metal blade three inches long attached to the same prong serves the purpose of a dipper to excite linear waves on the surface of the water (fig. 3).

Fig. 3.



The plane of the viewer being at right angles to the dipper, the ripples travel across the viewer normal to its plane.

Divergent light from an arc lamp after being collected into a parallel bundle by a collimating lens is incident obliquely to the water-surface. A porcelain trough (10 in. × 6 in. × 1½ in.) contains the liquid, and a box with glass sides covers the whole arrangement to keep the liquid surface clean. The trough and all other accessories are placed on a solid masonary pillar separated from the main floor to avoid extraneous vibrations which cause modifications of the ripple forms. The reflected beam of light passing through the viewer is obstructed by the wires, and an observer looking down the direction of light finds a stationary wave-form of the ripple on the vibrating wires. A camera is used in photographing these patterns on a magnified scale. The plane of the incident beam being normal to the direction of propagation of the ripples, the light reflected from the crests and troughs can thus be sharply focussed on a plane placed at right angles to this direction, whereas the light from the shoulders of the waves will be reflected in different directions; the wires of the viewer will not obstruct these beams, and this part of the wire image will be absent in the stroboscopic image focussed on the photographic screen. Even with very low amplitudes the image will appear diffuse. The picture, which shows the form of the ripples distinctly, could thus be secured only when the axis of the photographic lens makes an angle with the direction of the reflected light from the undisturbed water-surface. Under this circumstance the phenomena are similar to the appearance of a surface examined by Foucault arrangement. The entire field appears as a dull background on which

the stroboscopic shadow of the wire is indicated as a dense black sinuous curve, which is the representation of the form of the ripple on the liquid surface. With some care in the adjustment of the direction of the axis of the lens, this wavy pattern can be made of uniform density through the entire length of the picture. With very low amplitudes, however, some difference in the density still remains in the different parts of the curve (Pl. XXI.).

Any very slight impurity on the surface of water which lowers the surface-tension shortens the wave-length, producing a sharper inclination of the shoulders of the waves, and the density of the crests and troughs gets more and more deepened ; finally these portions only are visible. As suggested by Lord Rayleigh, the surface conditions have also been examined by observing the movements of camphor particles, and it has been found that the appearance of the form of the ripples on the screen is a clear indication of the nature of purity of the surface.

Another factor which modifies the form of the ripples is the size of the exciting blade. With the trough used the best size is three inches, and sizes smaller than that produce rounding of the edges of the linear ripples. This rounded character of the edges is easily seen by observing the surface with the help of a phonic wheel. Moreover, in this case the sinuous curve on the screen gets bent in the direction of the bends. With a bigger-sized blade the reflexions from the sides of the trough become very troublesome.

Another noticeable feature was the formation of streamer-like appearances from the surface of the exciter, which were very troublesome in the beginning. By auxiliary experiments it was found that the streamers were to a great extent due to (1) amplitude of the exciter, (2) the rigidity of fixing of the exciter, (3) the planeness and polish of the surface of the exciter in contact with the liquid, and (4) upon the nature of the material of which it was made. A dipper of glass was not found quite as satisfactory as one of brass. An exciter of pure silver with its surface optically worked and highly polished gave the best result ; an aluminium exciter carefully made was fairly good, but its surface had to be taken out and repolished from time to time.

As the amplitude of the ripples modifies the values of the surface-tension, leading to higher values with increased amplitudes, some preliminary observations were made to determine the maximum amplitude that could be used. It was found that the relation between the amplitude and the wave-length should be kept in the ratio of 1 : 6 in order to get a concordant result. To reduce the amplitude of the

ripples, the exciter was fixed at some distance from the viewer and closer to the base of the fork.

The question of the depth of the liquid is another factor which must be paid attention to. As has been pointed out by Lord Rayleigh in his paper cited above, it follows an exponential law, and for wave-lengths up to 4 mm. the depth has been kept more than 2 cm., and in this case the depth factor is negligible.

3. *Measurement of* λ, *n, and Results.*

A thin metal plate with two fine notches at a measured distance is fixed to the electromagnet driving the fork, and is placed so as to be in the same plane as the wires of the viewer and in a line with them, and this plate is photographed along with the curves. This gives the magnification of the system. The wave-lengths are measured on a Hilger cross-slide micrometer fitted with a low-power microscope so as to avoid bringing in the field of view the grains of the photographic plate. The individual readings differed only in the third place of decimals for a centimetre, which was further corrected by taking a group of five at a time.

The frequency of the fork was determined with the help of a Cambridge chronographic recorder tuned in unison with the fork, along with the records from an electrically-maintained standard clock beating seconds. The clock is checked every day with the help of a chronometer. The records are examined with a low-power microscope, and a cross-hair in the eyepiece and a number of coincidences are noted, and the frequency could thus be determined correct to the second place of decimals.

Conductivity water prepared in the Physical Chemistry Department was used throughout the experiment, and its conductivity was determined before and after the experiment to find out any change due to the action of the exciter. It was found that, though the conductivity increases slightly after two hours, it is negligible in half-an-hour, which is the time taken for each set of experiments.

The final result is tabulated as follows :—

"g" for Calcutta is taken as 978·815.

t°C.	ρ.	η.	λ in cm.	σ dynes/cm.
18·5	0·9985	93·69	·381	72·81
29·4	0·9958	95·71	·378	71·68
35·6	0·9948	93·81	·374	70·25
47·5	0·9992	93·92	·371	68·42
56·2	0·9852	94·01	·367	65·89
64·1	0·9811	94·11	·366	64·58

The temperatures were determined with a normal thermometer certified by the Physikalische Technische Reichsanstalt.

4. *Summary and Conclusions.*

1. A new stroboscopic arrangement has been devised for the determination of surface-tension of liquids by the method of ripples.

2. A new method of observing and photographing the form of the ripples has been devised. With the help of this arrangement a more accurate measurement of the wave-length of the ripples has been rendered possible.

3. The results that have been arrived at are fairly in agreement with the values of Weinstein and Volkmann, who used the capillary-tube method, but are lower than the values found by other workers using different methods.

Experiments are in progress to determine the surface-tension of different liquids at different temperatures, and also ripples of different frequencies.

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Calcutta.

CXII. *On Surface-Tension of Solids.*

By G. N. Antonoff, *D.Sc.* (*Manch.*)*.

IT appears at first sight that the surface-tension of a solid can be determined by measuring the breaking stress of a crystal. If the molecular structure of the substance is known, there are all the necessary data to calculate the surface-tension of a solid.

I tried to use the above method in order to find out the surface-tension of rock-salt, and found a value 1·4 dynes per cm., instead of 3000–4000 dynes per cm. as I expected from elementary theoretical considerations.

However, a crystal is never perfect, and apparently always contains some minute cracks ; there is always some doubt as to whether an experiment as above gives the desired information, although the breaking stress is as a rule a very definite figure varying within only a very narrow limit.

For this reason it is desirable to devise a method of measuring the field of force exercised by molecules in some other way. Before describing a method of this kind I must say a few words about surface-tension generally.

* Communicated by the Author.

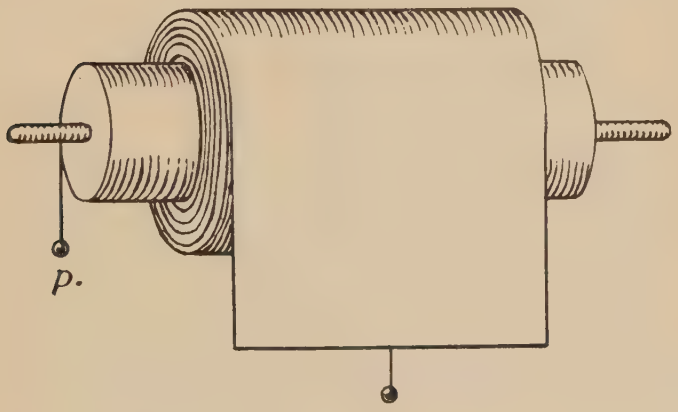
Definition of Surface-Tension.

The surface properties of liquids are such, as if the liquid mass was enclosed in a kind of membrane tending to contract under the effect of molecular forces. Some authors speak of it as of an elastic membrane, in the sense that it contracts and expands under the effect of external forces.

However, the surface properties of liquids do not altogether justify the above analogy. The elastic body expands proportionally to the force applied, whereas the liquid membranes expand in such a way that the acting force remains constant.

I can therefore propose the following mechanical model, which reproduces more accurately the characteristics of a liquid. Imagine a kind of roller blind (see fig. 1) with an

Fig. 1.



ideal membrane, *i. e.* whose thickness and weight = 0, and which moves without friction, (In this sense the drawing is not strictly correct, as it shows an appreciable thickness of the membrane.) If force is applied to the curtain, it will begin to unroll as soon as the applied force reaches a value slightly exceeding the force p, acting in the opposite direction.

Let l be the width of the membrane, and α the pull per unit width ; then

$$2l\alpha = p,$$

where p is the weight necessary and sufficient to produce stretching of the membrane.

It is seen that the expression for the work done in producing a unit surface is practically the same, viz.

$$pdx = 2l\alpha\, dx,$$

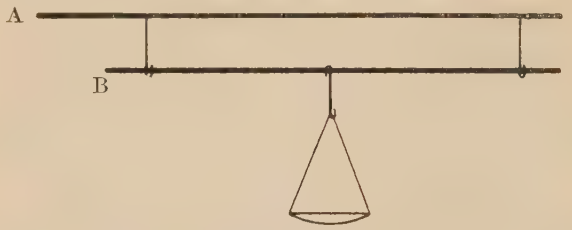
$$\int_0^h pdx = ph = \int_0^h 2l\alpha dx = 2l\alpha h,$$

where h is the vertical dimension of the film produced.

$$\therefore \quad \alpha = \frac{p}{2l}.$$

Thus the surface-tension defined as work is numerically equal to the same defined as force per unit width. (If the force p is not constant, as is the case in elastic bodies, the above expression cannot be integrated in the above way, and the expression for work is not identical with the expression for force.)

Fig. 2.



The above model can be reproduced in the following experimental device.

Imagine a thin rod A fixed horizontally (see fig. 2). If another rod B is placed in close contact with A, and they are both moistened with a liquid, they will adhere to one another. A certain definite weight must be applied to B in order to detach it from A, whereby a film of liquid will be produced between A and B.

Practically, in most cases, the formation of the film results in the breaking of the same. Thus, experimentally, the weight producing the breakage of the film is used for determination of surface-tension.

Such a method is very instructive as illustrating the surface-tension in a direct way, but it is seldom used and some other methods are generally preferred as more accurate. One of the drawbacks of this method is that the film always evaporates, and it is therefore not very suitable for working at different, and especially elevated, temperatures.

I describe this method somewhat in detail, because I shall soon make use of it under suitable conditions when it can render invaluable service.

Surface-Tension of Solids.

In certain cases one can devise a method of measuring the surface-tension of a solid, and it can be done on the following theory.

If a liquid rises in a capillary tube, it means that the cohesion between the particles of glass (or other material of which the capillary is made) and the liquid is greater than that between the particles of liquid.

If the surface-tension of the liquid is greater than that of the solid it is in contact with (as in the case of mercury-glass) the reverse takes place, *i. e.*, the liquid not only does not rise in the capillary, but there is a capillary depression, which is a measure of surface-tension just in the same way as capillary rise was a measure of it in the previous case.

Therefore it is necessary to find such systems whose surface-tension can be varied within the desired limits, in order to reverse the capillary action in a tube of material whose surface-tension is to be measured.

Thus, I took a capillary tube coated with paraffin inside. By placing it in water one can observe a marked capillary depression. On the other hand, I took a certain solution of isobutyric acid, whose surface-tension was known to me. This solution produced a definite rise in the same capillary.

By varying concentration of isobutyric acid one can notice that one intermediate concentration will produce neither capillary rise nor depression. The meniscus inside the capillary will remain on the same level as outside it.

This will happen just when the solution used has the same surface-tension as the material of the capillary.

As it is not easy to find this solution exactly, I experimented with several concentrations on either side of the point at which the capillary action is reversed, and determined the point by interpolation.

I thus found figures for paraffin and beeswax which are somewhat higher than the corresponding values found for these substances by the capillary method in the liquid state just above their melting-point.

These figures are quite reproducible, if the experiment is repeated with fresh material. But on standing there is always observed a marked change, *i. e.*, the liquid begins to wet paraffin as a result of a prolonged action, the capillary depression gradually diminishes and may change into capillary rise. This is either due to a kind of polarization produced in the solid by contact with liquid, or it may be a chemical action of some kind. Anyway, judging by the fact that figures obtained at first are of the order expected

from capillary determination of these substances above their melting-point, I believe these figures are characteristic, and not the ones observed as a result of prolonged action.

I shall give a few figures obtained by the above method for beeswax and paraffin.

Beeswax.

16 per cent. isobutyric acid (its surface-tension α=about 26 dynes per cm.) gave a rise in a capillary tube coated with beeswax of about 3 mm.

Pure water (α=72 dynes per cm.) gave a depression of about 4 mm.

The transition point, *i. e.*, the point at which there is no capillary rise or depression at all, corresponds to the concentration of acid about 9 per cent., having α=46 dynes per cm.

Another experiment with a different capillary gave:

16 per cent. solution ..... 8 mm. rise.
Water ..... 6 mm. depression.
Transition point at 9 per cent. of acid,

thus the surface-tension of beeswax=46 dynes per cm.

Paraffin.

16 per cent. solution of isobutyric acid . 6 mm. rise.
Water ..... 12 mm. depression.
Transition point at 10·7 per cent. of acid for which α=41 dynes per cm.

Another experiment with fresh coating gave the same figure with acid and 13 mm. depression with water, which gives a slightly lower figure for α, viz. α=40·4 dynes per cm.

So with fresh surfaces the experiment repeats itself fairly well, but on standing all values begin to change.

The limitations of this method are due to the chemical or dissolving action, which can always intervene and make the experiment impossible. But the other difficulty is to find systems whose surface-tension can vary within the desired ranges to suit the given solids.

The Surface-Tension of Glass and Rock Salt.

It is often assumed that glass is not a solid but rather a viscous liquid. Its tensile strength may vary within wide limits according to the conditions in which it was kept on cooling, and there is apparently an inevitable tendency to

form minute cracks which is responsible for a very low tensile strength generally observed experimentally.

However, all that is of no importance from the point of view of the method I am going to use to determine the surface-tension of glass. The fact is that glass does not change its shape during the experiment, and in this sense is like a solid. For measuring the surface-tension of glass I took advantage of the following facts.

Among the existing liquids we cannot easily find any suitable substances or mixtures of substances giving us values of surface-tension between 70 dynes per cm. (surface-tension of water) and 500 dynes per cm. (surface-tension of mercury).

Now I have come across certain substances of the nature of semi-fluids, which are capable of forming films of very high surface-tension. I can thus produce a system whose surface-tension may be varied at will within such limits as to cover the gap between the above figures.

To this end I have made the following experiments.

I acquired on the market two powderous substances, one being substantially lamp-black, and the other a blue pigment consisting substantially of ultramarine. Then I found that on mixing the above with some stable and non-volatile liquid, a paste can be obtained whose surface-tension can be measured by the method described on p. 1260.

Among the powderous substances I tried for the above purpose, there were bodies of a distinctly different nature, and only some of them were suitable for the purpose. I am not able yet to tell what this difference was due to, but it is quite real and can be shown in the following way.

I mix the lamp-black with some liquid, for example, salad oil—which is not volatile and is capable of forming pastes stable for many months.

The surface-tension of such paste can vary within wide limits, beginning from 3·5 dynes per cm. (surface-tension of pure salad oil), according to the proportion of the ingredients and their state of sub-division.

On the other hand the blue pigment, no matter how intimately mixed with oil, will always have a somewhat different appearance. It will not be as shiny as the other while being mixed. After mixing is finished, the impression is, as if oil comes out on the surface and forms a thin film. Measurements of surface-tension of this paste reveal a substantial difference as compared with the previous case. The figures obtained with the apparatus on p. 1260 do not show constancy. They differ little from those for pure oil,

and on standing generally give a figure identical with that of pure oil. I thought at first that this substance wanted a more intimate mixing and more prolonged grinding, but I found that it does not make any difference whatever. I do not know, as I have said, what this difference is due to, but substances of this kind are of no interest to me from the point of view of the object of this paper.

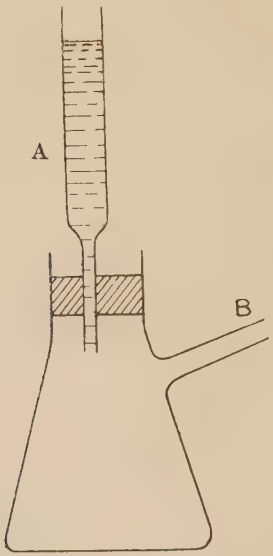
The paste formed by mixing the lamp-black with salad oil (or other suitable liquids), however, happened to be most suitable for measuring the surface-tension of glass and some other substances.

The actual experiment was done as follows.

Pastes of different concentrations were prepared and their surface-tensions measured by the apparatus of fig. 2.

The samples of the above paste are placed in tube A shown in fig. 3. This tube is joined to a thin capillary

Fig. 3.



and a suction applied at B. If the resistance in the capillary is sufficiently high, the paste slowly moves in the tube A downwards until the whole content of the tube A is driven into the flask.

By placing pastes of different concentrations into A one can observe the following :—

Sometimes the tube A on being emptied remains coated

with a thin film of the paste. In some other cases the paste does not adhere to the glass and descends as a result of suction, leaving behind a perfectly clean and transparent glass surface.

It can be seen that the pastes with low surface-tension generally wet the glass.

But when the surface-tension of the paste reaches a certain value, the paste ceases to wet the glass.

The experiment with pastes made of different substances and different liquids revealed always the same figure, viz. about 130 dynes per cm. for a given glass.

In another series of experiments with glass of a distinctly different chemical composition, I obtained a somewhat lower figure, but constant within narrow limits.

I assume that the paste wets the glass so long as its surface-tension is less than that of glass, and conversely, the surface-film does not adhere to the glass if the former has a higher surface-tension than the glass. The surface-tension of the paste at the transition point is therefore equal to the surface-tension of the glass.

Thus the figure 130 *dynes per cm. is the value of surface-tension of glass*, which does not depend upon such things as cracks in its surface, and is based on the measurement of the actual field of force exercised by the surface of glass. The figure obtained is of the order expected for a substance of the nature of fused salt.

In the experiment with paraffin there was observed a change in physical properties according to the duration of contact between the solid and the liquid.

It may be due to a kind of polarization, or dissolving action which, of course, would tend to upset the value of surface-tension thus obtained.

In the case of the above pastes in contact with glass no such changes were noticed by myself. Apparently the glass is not soluble in oil or its pastes, and I therefore believe that the above figure may be an accurate value of the surface-tension of glass.

The method is somewhat tedious, and it requires a lot of patience in order to find the transition point more accurately. In the case of paraffin it was possible to find the transition point by interpolation. In this case it is necessary to spend a lot of time in gradually approaching it from both sides.

In a similar manner I measured the *surface-tension of rock-salt and found it, as an average of several experiments, about* 315 *dynes per cm.* As these experiments present certain

difficulties, especially in case of rock-salt, I shall describe the actual experimental conditions more in detail, but I shall do so in a subsequent paper.

Conclusion.

In this paper I describe a method I devised for measuring the surface-tension of solids.

The method is not universal, but it can be used within a fairly wide range of values of surface-tension, provided no other factors intervene (such as solubility or other forms of action). I came to the conclusion that this method is suitable for measuring the surface-tension of mineral salts, which presents interest from the point of view of structure of crystalline matter as revealed by the X-ray method. I thus obtained certain values for glass and rock-salt.

The question may arise whether they actually represent the values of surface-tension, or whether they may be constants somewhat related to it. I have fully considered this point, but, taking into account the elementary theory, I do not think the constants can be anything else. However, I am going to discuss this point once again in a subsequent paper in which I shall describe in detail the actual experimental conditions.

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CXIII. *The Conductivity of Clouds dispersed from an Arc.* *By* H. P. Walmsley, *M.Sc.**

When an electric arc is produced between metallic electrodes in air, a cloud of fine particles is dispersed. In the case of easily oxidisable metals, such as cadmium, lead, copper, aluminium, and zinc, the particles consist of oxides; but platinum, silver, and gold yield metallic particles. Some of the particles are visible in the ultramicroscope and show marked Brownian movement. Hitherto, they have been of interest mainly in connexion with the quantitative study of Brownian motion and the validity of Einstein's formula for the displacement. By direct observation with the ultramicroscope, De Broglie [1] found for particles from arcs in which zinc, platinum, and silver electrodes were used, that some were charged positively, some negatively,

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

and others were neutral. Ehrenhaft and others have employed the charged particles in determinations of the charge carried by the electron. Most of the clouds produced by dispersal processes contain charged particles. De Broglie[2] has used particles in tobacco smoke, and from determinations of the mobility and the displacement produced by the Brownian movement, he obtained a value of $4{\cdot}5 \times 10^{-10}$ e.s.u. for e their charge. It thus appears that the charged particles usually carry the electronic charge, although for some of the larger particles De Broglie obtained larger values of e and concluded that such particles carried multiple charges. The presence of charged particles should give conductivity to the cloud, and the experiments of McClelland[3] on an arc between platinum electrodes show that this is the case. McClelland maintained an arc between the electrodes and passed a constant flow of gas past it into an ionization chamber, consisting of a cylindrical brass tube carrying two electrodes. He was able to measure the conductivity in different gases and under varied conditions and determine the mobility of the ions present. Since his paper was published, Ehrenhaft[4] found that the clouds produce coarse condensates, which settle out on the walls of the containing-vessel, and concluded that the particles first produced by the arc—the primary particles—coagulated as the cloud aged. Whytlaw-Gray[5] and others confirmed this by following the process quantitatively. If the charged particles of the cloud are liable to increase in mass by coagulation as the cloud ages, one would expect to find decreases in mobility and to find ions of different mobilities co-existing, even if the initial ions were all similar. McClelland[8] showed, in fact, that the mobility of the ions from platinum decreased as the distance between the arc and the electrodes was increased, other conditions remaining constant. It is clear, however, that by using his method, the process can be followed only over a short stage in the life of a cloud. The present experiments were undertaken to follow the process over a more extended period.

The Apparatus.

The experiments to be described were made on the clouds produced from an arc between cadmium electrodes. Cadmium was selected mainly on account of the ease with which it produces a cloud. The method of dispersal was identical with that described in detail by Professor Whytlaw-Gray[5].

The cloud chamber consisted of a closed galvanized iron

tank of about 850 litres capacity which was earthed. Two rectangular holes about a foot square were cut in opposite sides of the tank and were closed with $\frac{3}{4}$ inch plate glass to act as windows. The glass was held in a metal frame carrying lugs, which slipped over bolts fixed in the side of the tank and were secured by nuts. Rubber seatings were inserted between the glass and the frame and between the glass and the side of the tank which prevented fracture of the glass as the frame was bolted up and made the chamber air-tight. The chamber was filled with dry air free from dust and carbon dioxide, and was open to the outside air through a side-tube containing a cotton-wool filter and small sticks of caustic soda.

The cloud was dispersed by passing a direct current of 3 to 5 amperes between the cadmium electrodes for a few seconds and maintaining a draught across the arc by means of an electrically-driven fan. A steady stream of cloud was then drawn from the centre of the chamber through an ionization chamber and a flow-meter by means of a constant head aspirator. The ionization chamber consisted of a brass cylinder about 30 cm. long with a coaxial electrode protected in the usual way by a guard-ring. The electric field was applied by connecting the outer cylinder to one terminal of a battery of small accumulators, the other end of which was earthed. The current passing through the central electrode was measured by the rate of charging up of a Dolezalek electrometer, which was used at a sensitivity of 500–600 scale-divisions per volt.

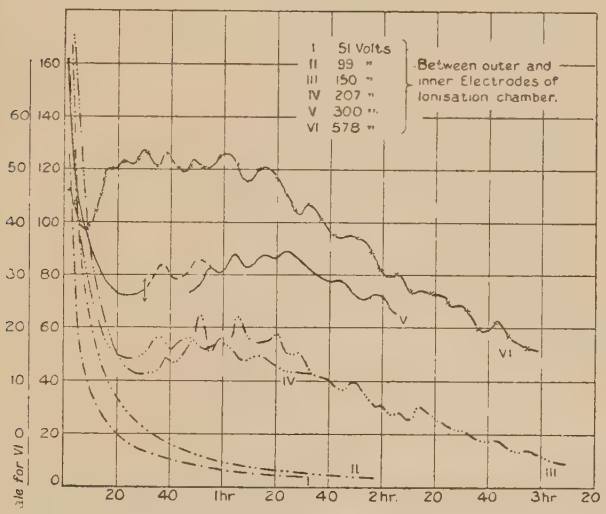
The Effect of Field Strength on the Ionization Currents.

Measurements of the ionization current were commenced as soon as possible after the production of the cloud and were continued until the current became negligibly small. The ionization curves therefore show the variation of the current with the age of the cloud. Ionization curves for clouds produced under approximately the same conditions were obtained with a series of different voltages on the ionization chamber. Some of these are reproduced in fig. 1. The currents are expressed in arbitrary units—scale-divisions per minute. The origin of time is taken at the commencement of sparking.

The group of curves shows several general characteristics, the most pronounced perhaps being the rapid fall in the current obtained during the first half-hour of the life of the cloud. All except two of the curves subsequently show

a tendency to rise, and when this happens the ionization curves become oscillatory. Oscillatory curves are not a

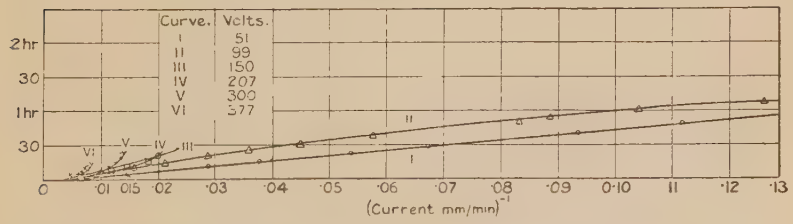
Fig. 1.



specific property of the clouds from cadmium. They have been obtained with clouds from zinc, aluminium, and arsenic, and are probably a general feature of oxide clouds dispersed in air.

Fig. 2 shows the curves obtained by plotting the reciprocals

Fig. 2.



of the current against age, for those portions of the curves which show the rapid fall. One of these is a perfectly straight line, one slightly convex to the axis of time, and the rest are concave to this axis. Since both positive and negative charges are present and rapidly disappear, there is a general agreement in these clouds with the law of recombination which holds for ions from Röntgen radiation. A

complete discussion of these curves is impossible without a knowledge of the source of the charges and the relative number of positive charges to negative. No experiments have yet been carried out on these questions, but indirect evidence has been obtained that the number of positive and negative charges are roughly equal for the cadmium oxide clouds. If we make the assumption that the positives are emitted by the hot metal electrodes and the negatives from the crust of oxide which is invariably produced on the electrodes by sparking, absolute equality in number is not to be expected. The effect of this inequality on the curves can be obtained as follows.

If n_1 and n_2 be the number of positive and negative ions per c.c. of the cloud, the law of recombination of ions, in the absence of any ionizing sources, gives

$$\frac{dn_1}{dt} = -\alpha n_1 n_2 = \frac{dn_2}{dt}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

whence

$$n_2 - n_1 = c \text{ (a constant)}. \quad . \quad . \quad . \quad . \quad (2)$$

So long as recombination only is operative, the difference between the number of ions of opposite signs remains constant, so the total charge per c.c. of cloud should remain unaltered with time. Assuming c positive, the preceding equation becomes

$$\frac{dn_1}{dt} = -\alpha n_1 (n_1 + c),$$

the solution of which is

$$\frac{n_1}{n_1 + c} = e^{-\alpha c(t-a)} = \frac{N_1}{N_2} e^{-\alpha c t}, \quad . \quad . \quad . \quad (3)$$

where a is a constant and N_1 and N_2 the number of positive and negative ions when $t=0$. Thus the ratio n_1/n_2 of the number of ions decreases exponentially with time. The recombination increases with c, which is to be expected, since the number of collisions favourable to recombination of the positive ions must increase with increasing numbers of negative ions. If N_2 is extremely great compared with N_1, the equation tends to the limiting form

$$n = N_1 e^{-\alpha N_2 t}.$$

This condition is approximately realized in the recombination of positively charged radioactive ions surrounded by the large number of ions produced by their radiations [6].

If we expand the exponential term, we can transform (3) into

$$\frac{1}{n_1} - \frac{1}{N_1} = \frac{N_2}{N_1}\alpha t + \frac{N_2}{N_1}c\left(\frac{\alpha^2 t^2}{2!} + \frac{\alpha^3 c t^3}{3!} + \ldots\right) \quad . \quad (4)$$

If $N_1 = N_2$ this reduces to the form

$$\frac{1}{n} - \frac{1}{N_1} = \alpha t. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If N_1 is unequal to N_2 this equation holds for small values of αt provided we replace α by $\frac{N_2}{N_1}\alpha$. Thus, if we plot reciprocals of the number of ions as ordinates and time as abscissæ, we obtain in the case of $N_1 = N_2$ a straight line of slope α and in the case of N_1 unequal to N_2, a curve convex to the axis of time, whose initial slope is N_2/N_1 times greater.

Returning to fig. 2, it is seen that the majority of the curves are concave to the axis of time, *i. e.*, that the charges disappear slower than the law of recombination in (1). The only remaining factor, in the absence of ionizing sources, influencing the rate of recombination is α, hence for these curves it is necessary that α decrease with time. It follows that in this stage of the cloud, either the collision frequency decreases or the fraction of collisions entailing disappearance of the cloud diminishes. If the Brownian motion of the ions obeys Einstein's displacement formula, the former assumption necessitates the mass of the ions increasing with time, either by coagulation or adsorption of matter from the medium. The second possibility might be realized if the particles adsorbed an insulating gas. Both effects may occur in the clouds.

Most of the clouds from cadmium electrodes give a reciprocal curve concave to the axis of time. With aluminium, however, at least half of the curves obtained are convex. The rate of disappearance of the charges in the first half-hour indicates that with the majority of clouds from cadmium, one at least of the following effects must occur:—

(*a*) There is a gradual increase in the mass of the ions as the cloud ages.

(*b*) The ratio of the number of collisions which result in recombination to the total number of collisions decreases with time.

(*c*) There is a production of ions in the cloud as it ages.

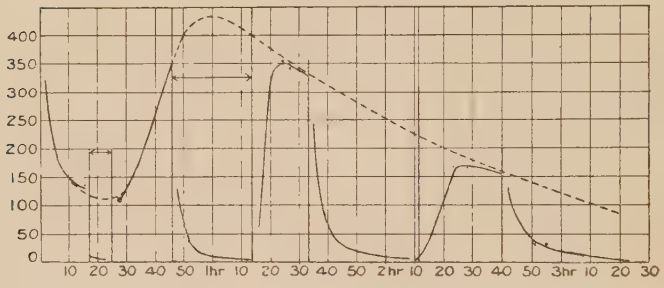
The direct measurements of mobility made by McClelland show that the mass of the ions from a platinum arc increases as the ions age.

Ionization Changes in Intense Electric Fields.

From fig. 1 the type of ionization-time curve is seen to depend largely on the electric field in the ionization vessel. With moderate to high fields, the ionization in this type of curve falls to a minimum at about half an hour and then rises to a maximum, which is followed by a slow fall. The increase in current persists at times for as long as three hours. Fig. 3 gives a more typical curve than any in fig. 1. In all cases the rise after the minimum is not a smooth curve but shows oscillations in the ionization. The weaker fields do not, in general, show this rise in current. We are, therefore, led to associate the rise with ions of low mobility, such as would pass practically uninfluenced through the weaker fields.

The ionization currents are a measure of the charge driven

Fig. 3.



by the field to the electrometer. Hence, before we can interpret the measurements in terms of the changes in the cloud, we must clearly distinguish between the changes in the ionization current, which are due to the action of the field, and changes which are due to ions in the cloud. If a number of ions are distributed initially throughout a volume V_0 and move under the influence of forces arising from external charges on electrodes of any shape, it is easy to show [7] that the motion is such that at any subsequent time all the ions are contained in a volume equal to V_0. Thus the electric field only changes the direction of motion of the ions, so that if a steady state is attained and n ions of like sign enter the field in unit time, the number of ions collected by the electrode is n and is independent of their mobility. Under these circumstances the changes in the ionization current are a measure of the changes in the ionization of the cloud

If, however, from some cause the mobility of the ions changed, their velocity in the electric field would alter. In the steady state the number received by the electrode per unit time will still be n, but the number of ions in motion in the field will change inversely as their velocity. The rearrangement of the ions within the electric field will cause additional ions to be driven to the electrode and will produce a temporary rise in the current through the electrode ; or, it will abstract ions from the incoming flow and produce a temporary decrease in the current through the electrode. Such changes in the ionization current may be considered as due to the action of the electric field. Temporarily we will neglect effects of this nature and assume that the currents measured are proportional to the ionization in the cloud.

Returning to fig. 3, it is clear, with this assumption, that there is a production of ions in the cloud subsequent to the first half-hour, and we have just seen that the new ions are ions of low mobility. The only obvious external agency producing ions within the cloud is the penetrating radiation of the earth. If n_s be the number of ions in the steady state when the number q produced per second by the radiation is equal to the number recombining per second, we have

$$n_s = \sqrt{\frac{q}{\alpha}},$$

so that the saturation current due to natural ionization of a cloud of ions in the steady state increases very rapidly with decrease in mobility. The number of ions produced by the radiation increases with time according to the formula (if $n=0$ for $t=0$)

$$n = n_s \tanh \sqrt{q\alpha}\, t.$$

The cloud will be approximately in the steady state when t is large compared with $1/2\sqrt{q\alpha}$, so that a considerable time may be necessary for the ionization to rise to a maximum. As $\sqrt{q\alpha}$ increases, n, which is proportional to the ionization current, approximates more and more rapidly to the value $\sqrt{q/\alpha}$. If q be constant, as will be the case if the ions in the cloud are produced by the penetrating radiation of the earth, the coefficient α must pass through a minimum and then increase, since the ionization current in fig. 3 passes through a maximum. This is highly probable, for the value of α determined in this way is an average value, so that it is only necessary for the heavier particles in the cloud to fall

out preferentially by precipitation under gravity, to account for the effect.

Ionization produced by the earth's penetrating radiation, however, does not appear sufficient to account for the magnitudes of the currents measured*. Hence there must be some other source producing ions. For these $\sqrt{q/\alpha}$ passes through a maximum and finally practically vanishes. Since the ions are of low mobility, it is quite unlikely that the maximum value which α can attain will be greater than 3400. its value for normal ions produced in air by, say, Röntgen radiation. Thus q must eventually decrease with time and vanish ; and, whatever changes α undergoes, the rate of production q of new ions in the cloud first increases to a maximum and ultimately decreases to zero.

* The number of ions per c.c. and their rate of production, q, on this hypothesis can be estimated as follows. The currents for curves 3, 4, and 6 of fig. 1, which are some of the weakest measured, rise to a maximum of between 50 and 60 scale-divisions per minute, corresponding to a rate of charging-up of the electrometer of about $\frac{1}{10}$ volt per minute. Taking the capacity as 60 cm., the current $i=3{\cdot}2\times10^{-4}$ E.S.U. If each ion carries unit charge the number of ions collected per second is $3{\cdot}2\times10^{-4}/4{\cdot}8\times10^{-10}=6{\cdot}6\times10^{5}$. The rate of flow of cloud through the ionization chamber was 4 c.c. per second, so that the number of ions per c.c. of the cloud is of the order of $1{\cdot}6\times10^{5}$. This is about one-tenth of the number of ultramicroscopical particles counted in similar clouds of the same age by Whytlaw-Gray (8).

If the ions arise from a source producing them at a rate q per second, the number of ions per c.c. of the gas increases with time according to the equation

$$n=\sqrt{\frac{q}{\alpha}}\tanh\sqrt{q\alpha}\,.\,t.$$

Thus n is equal to 98 per cent. of its equilibrium value $\sqrt{q/\alpha}$ when $t'=2{\cdot}3/\sqrt{q\alpha}$. In curve 6 of fig. 1, the time required is not likely to be greater than 20 mins., which makes $\sqrt{q\alpha}=\dfrac{2{\cdot}3}{1{\cdot}2}\times10^{-3}$. But we have seen that $\sqrt{\dfrac{q}{\alpha}}=1{\cdot}6\times10^{5}$ so $q=3{\cdot}2\times10^{2}$. Since q varies inversely as t', the precise value taken for t' makes little difference as regards the order of magnitude of q. Hence for the cloud in question, the ionizing source would have to supply at least 300 ions per c.c. per second to account for the effect. This is a hundredfold greater than the rate of production due to the earth's penetrating radiation. With denser clouds, there is no difficulty in obtaining currents at the maximum, a hundred times greater than in the example quoted, which suggests that the ionization must arise from processes occurring within the cloud.

Mobility Changes in the Cloud.

The preceding observations seem to indicate that the time of minimum ionization divides the electrical history of the clouds into two distinct parts. For convenience we will refer to the parts as the early stages and the later stages of the cloud. The reciprocal curves (fig. 2) show that in the early stages the changes in mobility of the particles are relatively gradual. The changes in the later stages will be found to be more marked, and can be described best by reference to a particular experiment (fig. 3). The field employed (400 volts on the ionization vessel) was sufficient with the rate of flow employed to give the saturation current for all ions of mobility greater than 1×10^{-4} cm./sec./volt/cm. Although ions of less mobility would not give a saturation current, yet these if present would contribute something to the current measured. The field, therefore, was sufficiently intense to deal with a number of particles of fairly low mobility.

From fig. 3 the ionization in the early stages is seen to drop rapidly to a minimum. The subsequent rise reaches a maximum and then falls away, the general course of the cloud being indicated by the dotted line. The vertical lines are drawn in pairs. At the time corresponding to the first line of a pair, the flow of cloud through the ionization chamber was stopped, and observations of the current due to the ions within the chamber continued. When this current died away, the flow of cloud was recommenced at the time indicated by the second line of the pair.

When the flow of cloud is steady, there is a distribution of ions in motion within the electric field, extending from one electrode to the other. Stopping the flow of cloud cuts off the supply of ions to the electric field, so that the subsequent current is due to the withdrawal of the ions which were between the electrodes at that moment. The curves in fig. 3 show that the times T required for the field to discharge these ions increase as the cloud ages. If we assume that there is no production of ions within the field, the time T is obviously the time required for the slowest moving ion within the gas to cross the electric field. In these experiments, unless T is greater than about 2 minutes (corresponding approximately to a mobility $k = 2{\cdot}78 \times 10^{-5}$), there is little chance of detecting this current at all; so the ions whose charges produce it must have mobilities which require at least two minutes to cross the field and are therefore large ions. Further, since T increases with the age of

the cloud, the mobility of the slowest moving ions in the cloud gradually decreases as the cloud ages.

The two rise curves which are taken after the time of maximum ionization conform with this view. The ionization current measured by the electrometer after recommencing the flow of cloud, will only attain a value proportional to the number of charges per unit volume of the cloud after a time T', which is, as before, determined by the time taken for the slowest moving class of ions in the cloud to cross the electric field. It is seen that the later curve requires a longer period to attain its maximum than the former, so that the largest type of ion present in the later one has considerably slower mobility than the slowest moving ions present at the earlier period of the cloud. The rise curve occurring before the time of maximum current would be expected on these grounds to rise still more rapidly, but it must be remembered that the effect here is masked to a certain extent by the disappearance of the small ions from the cloud.

We have yet to consider the effect on the curves of the production of ions, which has been shown to occur in the cloud. Since the effect of the electric field on the ions is merely to change their motion, it is clear that a production of similar ions at a point travelling with the ions will not alter the effect. If the field is sufficiently intense to produce saturation for ions of any mobility, a production of ions within the cloud will be indicated by a corresponding rise in the ionization current. Thus on recommencing the flow of cloud to the electric field, the time required for the current to attain its final value is independent of any production of charges within the cloud and is determined, as before, solely by the time required for the slowest moving ions present to cross the field. The two rise curves occurring after the maximum, therefore, still indicate the decrease in mobility of the slowest moving ions in the cloud at those times.

We have already shown that the rate of production of ions in the cloud passes through a maximum, and this is independent of assumptions as to what occurs to the coefficient of recombination α and consequently to the average value of the mobility of ions. We can therefore select pairs of times at either side of the maximum at which the rate of production q of ions in the cloud is the same for each pair. As the extreme case, we will assume that the fall curves are due entirely to ions which are produced from the cloud which is left within the ionization chamber when

the flow is stopped. For each pair the field removes all the ions from the cloud quicker at the earlier time than at the later time. Thus the ions produced at the earlier period must be more mobile than those produced later : so the fall curves show that the average mobility of the cloud decreases as it ages. The rise curves have shown that the mobility of the slowest moving ions decreases as the cloud ages, so both effects must take place concurrently. The effects due to ions in motion in the field when the flow of cloud is stopped conform with the effects due to the new ions produced in the field.

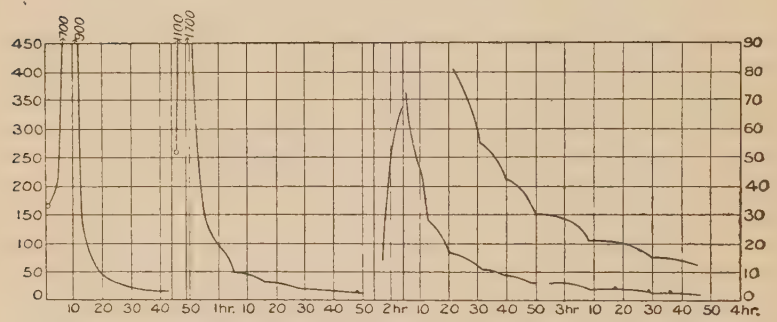
Returning to the experimental curve, it will be seen that after 20 minutes in the life of the cloud, the large ions do not contribute more than 10 per cent. and possibly not more than 5 per cent. of the total current obtained from the cloud at that time, whilst earlier the percentage is less. Thus as the cloud ages the number of large ions increases from a very small quantity to a maximum and then slowly decreases. The rate of production of new charges, therefore, is roughly proportional to the number of large ions in the cloud, and not to the number of small ions such as are responsible for the currents in the early stage of the life of the cloud. When new charges are produced in the cloud they appear mainly as large ions.

Variations with Mass of Material Dispersed.

The mass of material dispersed by the arc is obviously some function of the time of sparking and the current. By increasing either we obtain changes in the cloud. If we increase the amount of material dispersed, the mobility of the ions in the early stages, as judged by their rate of recombination, decreases. To compensate for the diminished mobility we can increase the field in the ionization chamber, as otherwise the currents become too feeble for measurement. With such clouds we may nearly eliminate the initial fall (Curve VI, fig. 1), or we may even obtain an ionization curve which commences to *rise* with time (fig. 4). The initial rise may be due to two causes. The ionization curve will rise with time provided the mobilities of the ions produced initially are sufficiently low. They will then require a long time to cross the electric field, and a corresponding time must elapse before the current becomes proportional to the volume density of charge within the cloud. But if the rate of production of new ions in the cloud, which gives rise to the minimum in fig. 3, is greatly increased, the

time at which it occurs will decrease. In consequence, a sufficiently great rate of production will tend to make the minimum disappear altogether and the ionization current will commence to rise with time. Such a curve, treated in the same manner as fig. 3, is shown in fig. 4. The field here removes all charged particles of mobility greater than 5×10^{-5}cm./sec./volt/cm.—the mobility of a spherical particle of radius $1{\cdot}1 \times 10^{-5}$ cm. which carries one electron and obeys the Stokes-Cunningham law. The last two rise curves show an increase in the size of the ions, since the slope of the former is more steep than the latter. The three fall curves disappear at diminishing rates. The last one is redrawn with ordinates magnified five times. Again, the rise of the initial curve, which, if due to the presence of large ions only, should be more rapid than the second, is

Fig. 4.



modified by the disappearance of ions due to recombination and by the growth of the large ions.

If there were no production of new ions in the cloud, the last fall curve would indicate that the large ions are present in groups. Suppose we had groups of ions present of gradually diminishing mobilities k_1, k_2, ... The times for these to cross the electric field are T_1, T_2, ... If now we fill the ionization chamber with a mixture of these types, and at time $t=0$ apply a field, the ions will move towards the electrodes giving a steady current until $t=T_1$. At this stage all ions of mobility k_1 will have been removed and the current will then drop and remain constant until $t=T_2$ and so on. We thus obtain a stepped curve. Diffusion of the particles and self-repulsion due to their charges whilst they are in motion in the field, will prevent the density changes at T_1, T_2 becoming abrupt, and will tend to smooth out the steps, making them concave to the time axis, which

is the shape of the last fall curve in fig. 3. The production of ions in the field during the decay of current complicates matters, and a complete explanation of the stepped curves requires more knowledge than we have yet obtained on the mechanism of the production of charges at this stage in the life of the cloud.

The Nature of the Ions.

It is seen from fig. 1 that a field of 99 volts on the ionization chamber, whilst collecting the majority of the smaller ions in the cloud, has little appreciable effect upon the large ions. Since this field is sufficient to produce saturation currents for ions of mobility as low as $4{\cdot}0 \times 10^{-4}$ cm./sec./volt/cm., the large ions in general must be less mobile than this and the small ions more mobile. The mobility of the slowest moving ions in the cloud at any time can be determined if we know the time T, required for them to cross the electric field. With the usual notation the mobility

$$k = \frac{1}{2\,\mathrm{TV}}(b^2 - a^2)\log_e \frac{b}{a}, \quad . \quad . \quad . \quad . \quad (6)$$

where V is the voltage applied to the ionization chamber. Since the large ions cannot be detected by the method of stopping or restarting the flow of cloud through the ionization chamber until the cloud is about 20 minutes old, the earlier values of T must be less than 2 minutes, corresponding to a mobility greater than $2{\cdot}8 \times 10^{-5}$. We have seen that the value T can be obtained from the rise curves of fig. 3, even if a production of new ions is taking place in the cloud. For these curves an approximate value of T is good enough to give the order of magnitude of the mobility since the product $k\mathrm{T}$ is a constant. For the two rise curves after the minimum we may take T as 10 minutes and 20 minutes respectively, which lead to values of k equal to $5{\cdot}6 \times 10^{-6}$ and $2{\cdot}8 \times 10^{-6}$. Since, moreover, we have both small ions and large ions present in the cloud at all times (as is shown by the curves of fig. 1 for the various field strengths), the shape of the rise curves indicates that we must have ions present in the cloud with varying mobilities between those of the small ions and that of the slowest moving ions present. If this were not so and the ions in the cloud were grouped about comparatively few characteristic mobilities, the rise curves would be stepped and not smooth. The times of occurrence of the steps would give these characteristic mobilities.

It therefore appears that in the initial stages of the cloud the ions present are relatively fairly mobile, but as the cloud ages new ions appear with continuously diminishing mobilities and the process continues until the ionization currents become too weak to be measured.

If we knew the shape of the ions it might be possible to determine their size. We can obtain some idea, however, by determining the size of a spherical particle of the same mobility carrying a charge equal to that of the electron, by means of the Stokes-Cunningham equation. The radius a of the particle is given in terms of the mobility k, the coefficient of viscosity η, and the mean free path of the gas molecules λ, by

$$a = \frac{e}{6\pi\eta k}\left(1 + \cdot 817\frac{\lambda}{a}\right). \quad . \quad . \quad . \quad . \quad (7)$$

Taking $e = 4{\cdot}77 \times 10^{-10}$, $\lambda = 7{\cdot}5 \times 10^{-6}$, and $\eta = 1{\cdot}78 \times 10^{-4}$, its value at 15° C.,

$$a = \frac{4{\cdot}74}{k}\left(1 + \frac{6{\cdot}13 \times 10^{-6}}{a}\right) \times 10^{-10}\ \text{cm}. \quad . \quad . \quad (8)$$

The value $k = 4{\cdot}0 \times 10^{-4}$, the lower limit to the mobility of the small ions, gives $a = 3{\cdot}35 \times 10^{-6}$ cm. This then is the upper limit to the size of the ions responsible for the initial rapid fall in the ionization current.

Whytlaw-Gray and Speakman [8] from direct counts and microbalance determinations of mass, estimate the average size of the ultramicroscopic particles in the initial stages of similar clouds as spheres of radius $5{\cdot}0 \times 10^{-6}$ cm. The agreement is sufficiently close to show that the small ions of these clouds are actually charged particles of ultramicroscopic size. Since amicrons seem to be always present initially, in relatively large numbers, a small proportion of amicrons carrying charges will suffice to account for the difference in values obtained by the two methods.

At 20 minutes in the life of the cloud of fig. 3, the large ions have mobilities greater than $2{\cdot}8 \times 10^{5}$ corresponding to a radius $a = 2{\cdot}2 \times 10^{5}$ cm., and the limiting mobilities from the rise curves $k = 5{\cdot}6 \times 10^{-6}$ and $k = 2{\cdot}8 \times 10^{-6}$ correspond to particles of radius $9{\cdot}11 \times 10^{-5}$ cm. and $1{\cdot}76 \times 10^{-4}$ cm.

If we compare the volumes of the ultramicrons forming the small ions with the volumes of the particles constituting the large ions, it seems very clear that the large ions must arise by the coagulation of large numbers of ultramicrons.

The general decrease of mobilities throughout the life-history of the cloud shows that, so far as the charged particles are concerned, there must be a gradual decrease in the number of particles per unit volume of the cloud due to a process of coagulation. This is in complete agreement with the deductions of Whytlaw-Gray from totally different evidence, and is clearly brought out by the remarkable series of photo-micrographs of deposits from arc clouds which he has published.

Summary.

Types of ionization curves obtained from cadmium oxide clouds produced in dry air free from dust and carbon dioxide by an arc discharge, are described. In the later stages of the cloud the ions present at any time are not of uniform mobility. The average mobility of the ions in the cloud and the mobility of the slowest moving ions present at any time diminish as the cloud ages. The dimensions of the ions and the dimensions of the particles in the clouds are of the same order of magnitude, which indicates that the ions are the charged particles of the cloud. The changes in mobility show that coagulation of the particles occurs as the cloud ages.

Under certain circumstances, the ionization curves after decreasing owing to recombination of ions, subsequently show a rise in current strength and become oscillatory. On the usual assumption that the ionization current is proportional to the ionization in the cloud, this indicates that a production of new charges occurs as the clouds age. The new charges appear mainly on particles of low mobility.

My thanks are due to Professor R. Whytlaw-Gray both for proposing the research and for the interest he took in the progress of the work. To Professor W. L. Bragg I am indebted for much constructive criticism.

The Physical Laboratories,
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CXIV. *Some Experiments on Hydrogen Over-potential at a Mercury Cathode and a Discussion of their Bearing on Current Theories.* *By* A. L. McAulay, F.Inst.P., *and* F. P. Bowden, *M.Sc.**

THE following is an account of some experiments on hydrogen over-potential at a mercury cathode with mixed electrolytes containing metal and hydrogen ions.

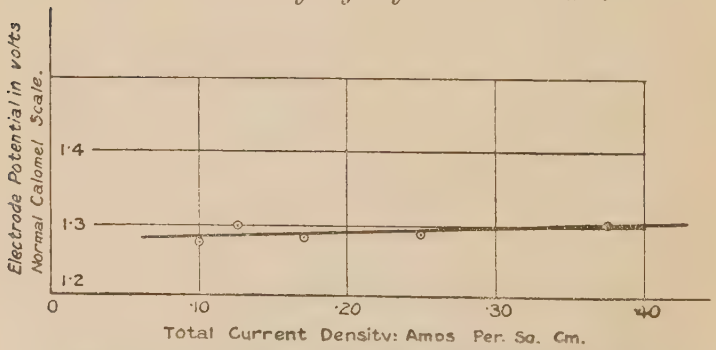
These experiments provide information which is used in a critical discussion of theories of over-potential.

Experiments and Results.

The experiments were essentially measurements by the direct method of the over-potential at zinc and mercury surfaces using an electrolyte composed of varying proportions of sulphuric acid and zinc or mercury sulphate, together with periodic weighings of the cathode to determine the relative amounts of current carried by metal and hydrogen ions. Their object was to investigate the relations between the over-potential, the total current passing through the cathode surface, and the current conveyed to the surface by hydrogen ions only.

The results of these experiments lead to two general conclusions. First the magnitude of the over-potential is determined only by the current carried by the hydrogen ions and the nature of the cathode, and is almost independent of the total current flowing. The figure shows how nearly

Electrode Potential against Total Current Density
Current carried by Hydrogen Ions Constant.



true this is. Here the single electrode potential at a mercury cathode on the normal calomel scale is plotted against total current density. The electrolyte consisted of a different mixture of sulphuric acid and zinc sulphate for

* Communicated by the Authors.

each point on the graph. It was so adjusted that the current carried by the hydrogen ions was in every case very nearly ·1 amp. per sq. cm. The left-hand point was obtained with pure acid as electrolyte. It will be seen that with an over-potential of about 1·0 volt for a range of total current density of nearly 1 to 4 there was only a variation of about 2 per cent. in the over-potential. With a mercury cathode it is possible to obtain measurements reproducible within a few millivolts. If similar experiments be made with solid cathodes the variations in the nature of the surface give large secondary effects, some irregular, and some, more dangerous, systematic. Effects due to such causes as pitting from corrosion by acid and repair of the surface by plating are large.

The second general conclusion is that when an over-potential film is established metals deposit at a potential characteristic of hydrogen, although before the film forms they may deposit at much lower potentials from the same electrolyte. This is not due to low concentration of metal ions in the neighbourhood of the cathode. Stirring has no effect. The phenomenon may be observed with a mercury salt in solution, in which case a high over-potential appears suddenly with no change in current density or other external conditions *, and both mercury and hydrogen deposit at a cathode potential 1·5 volts more negative than that at which mercury was being deposited an instant before.

It appears, therefore, that the mercury ions play no primary part, either as constructive or destructive agents, in the production of the over-potential film, but that the film hinders their deposition in such a way that the work required to convey unit charge across the cathode boundary is the same whatever ions convey the charge.

The magnitude of the change in the free energy of the metal on deposition (which is measured by its reversible deposition potential) does not affect the cathode potential when the film is present, although a large part of the current is being carried by the metal ions.

Discussion of Theories.

1. *Ohmic Resistance Theory.*—The above experiments are obviously extremely hard to explain on this theory, as they seem to show that the over-potential is actually independent of the current density.

2. *Active Film Theory.*—The experiments can be explained by the presence on the cathode of a layer of an active modification of hydrogen, such as monatomic hydrogen, provided

* McAulay and Bowden, Proc. Roy. Soc. (read Feb. 25, 1926).

that the velocity of evaporation of hydrogen ions is much greater than that of the supply of metal ions. If this is so it will be possible for the hydrogen film of high free energy to maintain its over-potential, and the excess energy forced upon the metal ions will appear as kinetic energy which will be dissipated as heat as the cathode is bombarded. However, the results obtained with a cathode-ray oscillograph by Newbery* advance an argument against this theory. Newbery's photographs show that the disappearance of the greater part of the over-voltage takes place in an interval small compared with a thousandth of a second, whereas, if the layer of active hydrogen were even one atom thick the time required for its dissipation would be expected to be considerably greater than this.

3. *Desorption Theory.*—A theory similar to that suggested by Rideal† in 1920 appears to fit many of the facts in a satisfactory way. Rideal proposed that over-potential might be due to the work required to desorb hydrogen molecules which were adsorbed to the cathode surface, covering it with a continuous layer, and preventing the deposition of further ions. Evidently the work required to desorb a molecule of adsorbed hydrogen should be independent of the nature of the desorbing ion, and so it would appear natural that both hydrogen and metal would be deposited simultaneously and non-preferentially. The difficulty arising from the fact that the metals investigated were divalent may be explained in more than one way. The following suggests itself as plausible. The abstraction of two electrons from a surface on which an over-potential film is established may necessitate the desorption of two atoms, because metallic conduction does not exist in the film, and the desorbing ion can only detach the electron which attaches the adsorbed atom. A single atom may be desorbed by a hydrogen ion.

This theory evidently indicates that during the adsorption of the hydrogen atoms a current should flow on to the cathode at a potential very much lower than that necessary for bubble formation at atmospheric pressure, for the adsorbed film must have a low free energy. To form a monomolecular layer a quantity of electricity of the order of 10^{-3} coulomb must flow on to the cathode. In experiments with a pure normal acid electrolyte and a current density of about 10^{-5} amp./cm.^{2}, it was found that the single electrode potential at a mercury cathode increased with time from potentials of about $+\cdot4$ on the calomel scale.

An objection to the theory arises from the fact, frequently

* Newbery, Proc. Roy. Soc. cvii. A (1925).
† Rideal, Journ. Am. Chem. Soc. 1920.

observed by the writers, that when a large current (1 amp. per sp. cm.) is passed through pure normal acid to a mercury cathode an over-voltage of more than ·5 volt remains after the circuit is opened. This over-potential decays at different speeds according to circumstances, but some continues to exist for a time of the order of minutes. Some of Newbery's photographs also indicate the existence of this effect.

4. *Slow Transformation of a Product between* H *and* H_2.—The effect just discussed, that is the persistence of an over-potential on open circuit, renders it difficult to maintain a theory which ascribes over-potential to a high concentration produced by the slowness of some stage in the transformation of hydrogen ions to hydrogen gas.

The above discussion finds some objections to all the usual theories of over-potential. Many of these objections, however, are not fatal. They seem to be least serious in the case of that which supposes that a film of high free energy is formed and behaves as an electronegative cathode. It may be that this theory, combined with the desorption theory to account for the very rapid first fall of potential on opening circuit, will be thought to be most acceptable. It is intended to carry out further experiments on the lines suggested above, with a view to narrowing further the theoretical possibilities.

Summary.

It is shown that the over-voltage at a mercury cathode with a mixed electrolyte containing acid and metallic salt is independent of the total current flowing. It is the same for large ranges of total current if the current carried by the hydrogen ions is the same in each case.

When over-voltage is established, hydrogen and metal are both deposited at a high potential characteristic of hydrogen, whatever the reversible potential of the metal.

Four theories which have been advanced to explain over-potential are discussed in the light of these and other experiments. It is shown that the evidence is strongly against the theory which accounts over-potential the result of an ohmic resistance, and also against that which supposes it to be due to a high concentration produced by the slowness of a stage in the transformation of hydrogen ions to hydrogen gas. It is suggested that a combination of the theory of an active film of hydrogen or hydride, whose high free energy provides part of the over-potential, with the view that a further over-potential is necessary for the desorption of this film might explain all the known facts.

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CXV. *Note on the Second Law of Thermodynamics.* By W. F. Sedgwick, *M.A.**

As is well known, W. Thomson expressed the second law of Thermodynamics, in his paper "On the Dynamical Theory of Heat" (Trans. R. S. Edin. 1851, vol. xx. p. 265; or Math. and Phys. Papers, i. p. 179), in the following terms:—

"It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."

In his review of the second edition of Tait's 'Sketch of Thermodynamics,' 1877 (Nature, 1878, vol. xvii. p. 279; or Scientific Papers, ii. p. 669), Maxwell took exception to this statement of the law, remarking that—

"Without some further restriction this axiom cannot be considered as true, for by allowing air to expand we may derive mechanical effect from it by cooling it below the temperature of the coldest of surrounding objects."

Maxwell goes on to state that—

"If we make it a condition that the material agency is to be left in the same state at the end of the process as it was at first, and also that the mechanical effect is not to be derived from the pressure of the hot or of the cold body, the axiom will be rendered strictly true, but this brings us back to a simple re-assertion of Carnot's principle, except that it is extended from heat engines to all other kinds of inanimate material agency."

By the statement that with the suggested alteration the axiom merely amounts to a re-assertion of Carnot's principle, Maxwell presumably means that the revised axiom merely lends itself to the completion of the familiar proof of the maximum efficiency of the reversible engine, in which the supposed more efficient irreversible engine drives the reversed reversible engine, drawing the same heat from the source that the reversed engine returns to it; with the result that work would be done at the expense of heat drawn from the refrigerator, contrary to the axiom, which asserts such an operation to be impossible by any "inanimate material agency." Even so it may be remarked that if the axiom, with Maxwell's limitations, is sufficient for the establishment of Carnot's principle, it has served its main purpose.

But with regard to Maxwell's criticism of Thomson's form of the law, it will be observed that in the case which he brings forward as conflicting with that law the work is done at the expense of the intrinsic energy of the expanding and

* Communicated by the Author.

cooling air (Thomson's "portion of matter"), and that no heat is actually withdrawn from the air to any other of the surrounding objects, *e.g.* to a working heat engine. In fact the air may be said to cool itself in the process of doing work. It seems highly probable, however, that in using the words "by cooling it" Thomson intended them to be taken in the transitive, or active, sense which they naturally bear; and that what he had in mind was the actual withdrawal of heat, in the form of heat, from the "portion of matter" (*e.g.* the refrigerator) by another body (*e.g.* the heat-engine), and its subsequent conversion into mechanical effect by this second, independent body. Taken in this sense, Thomson's form of the second law appears to be true, as an expression of a fact of experience (*cf.* Silvanus Thompson's 'Life of Lord Kelvin,' 1910, p. 284). It formulates a limitation which we should expect to hold good on the theory that differences of temperature are due to differences in the average kinetic energy of translation of the molecules of a body, and that accordingly equality of temperature between two bodies is only attained when the average kinetic energy of translation of the molecules within one of the bodies is in equilibrium with the average kinetic energy of translation of the molecules in the other. For under such conditions, although groups of molecules in one body may from time to time impart heat or energy to groups of molecules in the other body which at the time have less energy of motion, such an effect would not occur on the average, or for any appreciable amount of time, having regard to the enormous, though still finite, number of molecules concerned (*cf.* Maxwell, *l. c.* pp. 670–1). Consequently we should not expect that it would be possible to extract heat from any portion of matter unless there were some body in the neighbourhood at a lower temperature, however small the difference, than the matter in question; if two bodies started at equal temperatures, the transference of heat from one to the other would immediately and necessarily begin to involve the impossible result of a transference of heat from the colder to the hotter.

In Maxwell's expanding and self-cooling air-piston there is no actual transference of heat to any external body, whether cooler or hotter; but the energy of motion of the molecules of the air is merely drawn on to cause the piston to move against an external resistance which is at first, at all events, necessarily smaller, when all the forces are taken into account, than the resultant pressure due to the air in the piston; and there is nothing in the molecular theory in conflict with the supposed motion of the piston.

In order to preclude the construction placed upon it by Maxwell, it is suggested that Lord Kelvin's form of the Second Law of Thermodynamics might be modified so as to run as follows:—

It is impossible, by means of inanimate material agency, to derive mechanical effect through a direct transference of heat, in the form of heat, to another body from any portion of matter which is at or below the temperature of the coldest of the surrounding objects.

In the third edition of Preston's 'Theory of Heat,' as revised by J. R. Cotter, 1919, it is stated (Art. 324, p. 684) that Prof. W. M'F. Orr has devised the following alternative form of Lord Kelvin's axiom, viz. :—

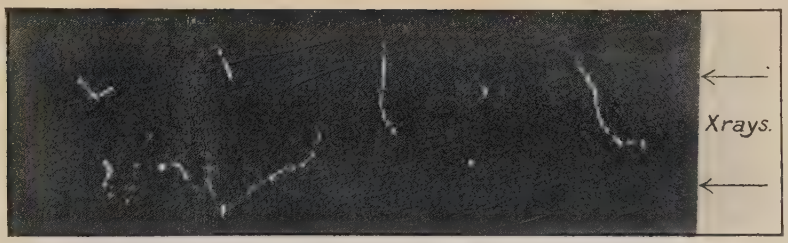
"If a system interchanges heat with external bodies *at one assigned temperature only*, then it is impossible that *in a cycle* it should, on the whole, receive heat from external bodies, and (as a necessary consequence by the first law), on the whole, do work on external bodies."

In this form the law would apply to the higher as well as to the lower of the two temperatures in an ordinary cycle ; the actual transference of heat at the lower of the two temperatures being annulled, in the complete cycle contemplated in the revised axiom, by the superposition of two opposing cycles, in the customary manner. The axiomatic character of the law when applied to the higher temperature is, however, by no means so obvious as in the case of its application to the lower temperature. Moreover, there appears to be no sufficient reason for the complication of Lord Kelvin's form of the second law by the introduction of the idea of a cycle ; provided the axiom is restricted, as suggested above, so as to apply only to operations involving a direct transfer of heat.

On the same page of Preston's book there is also given a revised form of Clausius' expression of the second law, likewise due to Prof. Orr. But Clausius' "rather dubious axiom" (as Tait describes it in § 53 of the first edition of his 'Sketch of Thermodynamics,' 1868), besides being inherently less axiomatic than Lord Kelvin's, also labours under the disadvantage, as compared with the latter, of necessitating the consideration of two temperatures instead of one only, and that the lowest. For these reasons it seems preferable to found the theory on Lord Kelvin's axiom, which connects itself with, and is indeed almost a deduction from, the kinetic theory of heat, in a manner which could not be claimed for its rival form.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

1.

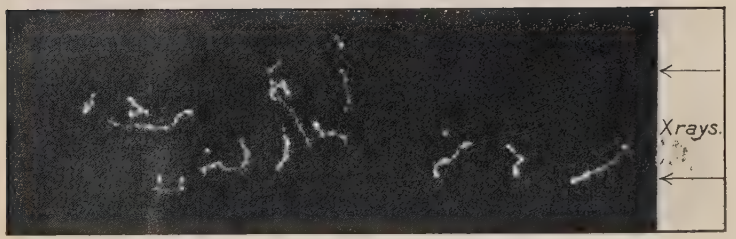


AIR. $\lambda = \cdot 57$ Å

2.

AIR. $\lambda = \cdot 35$ Å.

3.

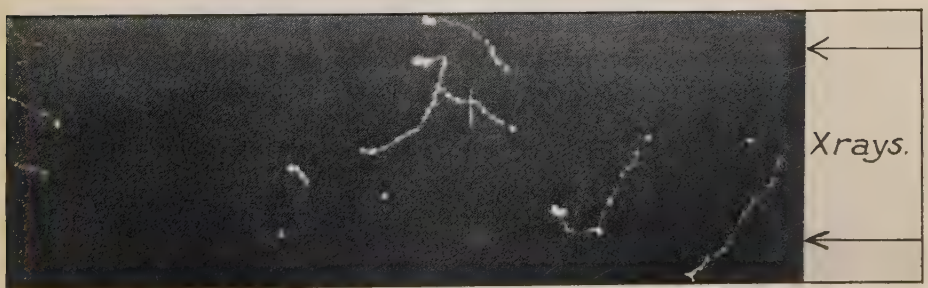


OXYGEN. $\lambda = \cdot 709$ Å.

4.

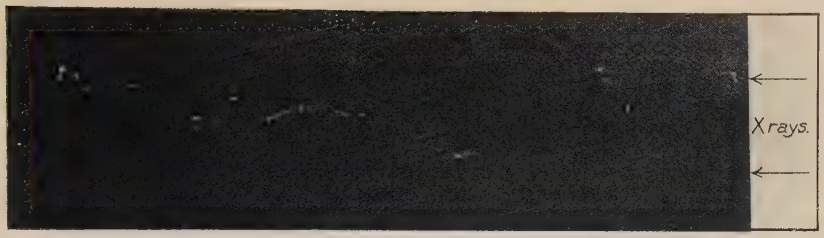
OXYGEN. $\lambda = \cdot 614$ Å.

5.



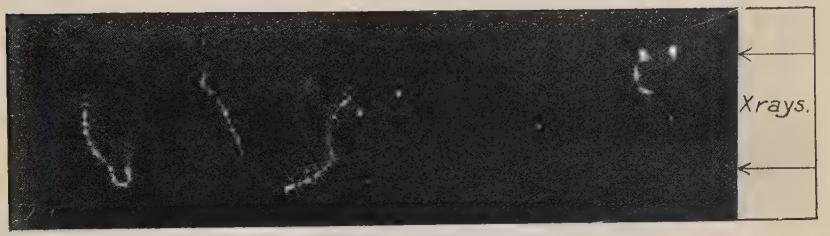
OXYGEN. $\lambda = \cdot 514$ Å.

6.



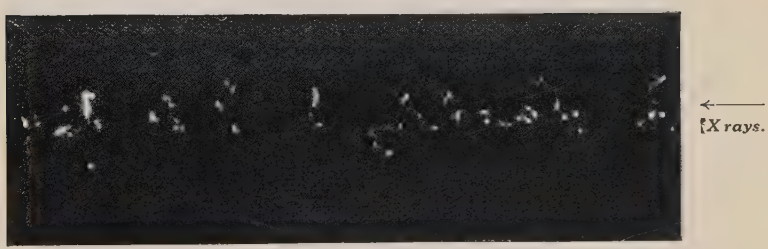
NITROGEN. $\lambda = \cdot 614$ Å.

7.



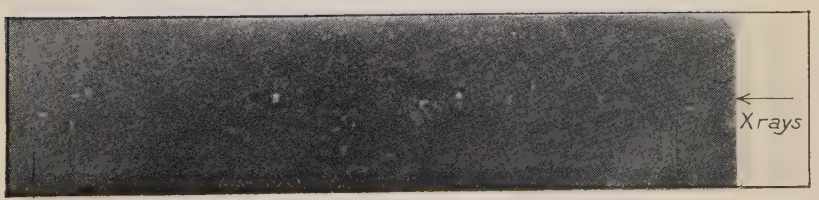
NITROGEN. $\lambda = \cdot 545$ Å.

8.



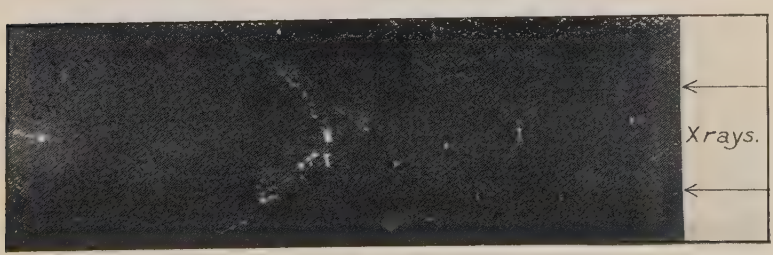
ARGON. $\lambda = \cdot 614$ Å.

9.

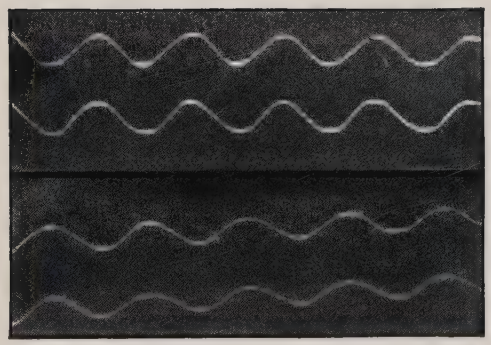


HYDROGEN. $\lambda = \cdot 614$ Å.

10.



HYDROGEN + 1 % ARGON. $\lambda = \cdot 614$ Å.



INDEX TO VOL. L.

ABSORPTION spectra, on, 726; on the, of vapours of Zn, Cd, Pb, Sn, Bi, and Sb, 732.

Acids, on the melting-points of the normal saturated dibasic, 944.

Addenbrooke (G. L.) on the connexions between the dielectric and other physical properties of non-metallic elements, 225.

Adsorption equation, on an experimental verification of Gibbs', 641.

—— of ions on colloidal particles, on the, 32; on the, of gases by activated charcoal, 109, 659, 1042.

Air, on the production of delta-rays in, 1.

Air-bubble viscometer, on the, 395.

Air-currents in pipes, on a thermionic valve method of measuring the velocity of, 1117.

Allen (A. O.) on lines of maximum stress in mild steel plates, 1039.

Alpha-rays, on the delta-rays produced by, 1.

Aluminium, on the absorption spectrum of, 451; on the solubility of hydrogen in, at high temperatures, 510.

Anatase, on the crystal of, 1153.

Anisotropy of some inorganic gaseous compounds, on the optical, 491.

Antimony, on the absorption spectrum of the vapour of, 742.

Antonoff (Dr. G. N.) on evidence of molecular changes in vapours and liquids, 1121; on the surface-tension of solids, 1258.

Arc, on the conductivity of clouds dispersed from an, 1266.

——, on the low voltage, in cæsium vapour, 705; on enhanced lines produced by the interrupted, in sodium and potassium vapours, 721; on the sodium, in a vacuum, 940.

Archer (C. T.) on the variation of the thermal conductivity of gases with pressure, 593.

Argon, on the production of delta-rays in, 1.

Artificial line, on the generalized, 553.

Atmosphere, on the energy in the, 523.

Atoms, on the statistical mechanics of assemblies of ionized, 845; on the time of excitation of hydrogen, 1082.

Bailey (E. B.) on the geology of the Island of Mull, 558.

Baker (J. F.) on the determination of minima maxima forces in problems of dynamic balance, 635.

Banerji (D.) on the determination of surface-tension by the method of ripples, 1252.

Barkla (Prof. C. G.) on the superposition of X-rays and on scattering, 542.

Barr (Dr. G.) on the air-bubble viscometer, 395.

Bartlett (A. C.) on the generalized artificial line, 553.

Barton (A. W.) on the efficiency of beta-ray recoil of radium C from radium B, 835.

Barytes, on the intensity of reflexion of X-rays by, 897.

Bell (E. T.) on certain functions of two variables, 304.

Belz (M. H.) on the distribution of energy in the continuous X-ray spectrum, 50.

Benzene solutions, on the dielectric constants of, 1035.

Beta-ray recoil of radium C from radium B, on the efficiency of, 835

Beta-rays associated with scattered X-rays, on the, 1217.

Bircumshaw (L. L.) on the solubility of hydrogen in tin and aluminium at high temperatures, 510.

Bismuth, on the absorption spectrum of the vapour of, 732.

Bloch (L. & E.) on the water-spark absorption spectrum of iron, 704.

Books, new:—Joly's The Surface-History of the Earth, 893; Millikan's The Electron, 894; Lewis's System of Physical Chemistry, 894; Schuster and Lees's Exercises in Practical Physics, 894; Appell's Sur une forme générale des équations de la dynamique, 895; Valiron's Fonctions entières et fonctions méromorphes, 895; Appell's Séries hypergéométriques de plusieurs variables, 895; Brown's Higher

Mathematics for Students of Engineering and Science, 1215; Silberstein's Vectorial Mechanics, 1215; Hobson's Theory of Functions of a Real Variable and t e Theory of Fourier's Series, 1215; Cullis's Matrices and Determinoids, 1216; Bromwich's Introduction to the Theory of Infinite Series, 1216; Baker's Principles of Geometry, 1216.
Bowden (F. P.) on hydrogen overpotential at a mercury cathode, 1282.
Bragg (Prof. W. L.) on the intensity of reflexion of X-rays by crystals, 897.
Brown (Prof. A.) on the application of the rigorous quotient theorem, 748.
Brunt (D.) on the energy in the earth's atmosphere, 523.
Burch (C. R.) on the quantitative theory of induction heating, 768.
Burgers (W. G.) on an X-ray examination of *i*-erythrytol, 289.
Burnside (W.) on the hypothetical infinite population of theoretical statistics, 670.
Burton (Prof. E. F.) on the relation between temperature and minimum sparking potential, 219.
Cadmium, on the absorption spectrum of the vapour of, 732; on a method for exciting the spectrum of, 752.
Cæsium vapour, on the low voltage arc in, 705.
Calcium, on the scattering power of, for X-rays, 1202.
Callis (C. D.) on the resistance of a condenser at radio frequency, 428.
Cameron (W. H. B.) on the production of spectra of carbon, oxygen, and nitrogen in the presence of neon, 405.
Campbell (Dr. N. R.) on the evacuation of carbon dioxide and water, 762; on time and chance, 1106; on dimensional analysis, 1151.
Carbon, on the production of the spectrum of, in the presence of neon, 405; on the structure of the atom of, 809.
—— dioxide, on the adsorption of, by activated charcoal, 116, 126, 659; on the evacuation of, 762.
Carbon monoxide, on the adsorption of, by activated charcoal, 116, 126, 659, 1042.
Cassiterite, on the crystal of, 1169.
Chadwick (Dr. J.) on the delta-rays produced by alpha-particles in different gases, 1.
Chance, on time and, 1106.
Charcoal, on the adsorption of gases by activated, 109, 659, 1042.
Chemical action, on the nature of the critical increment of, 606.
—— affinity, on the forces of 786.
Chromatic emulsions, on the optical properties of, 321.
Clifford (G. H. W.) on the application of Saint-Venant's principle to frameworks having redundant bracing members, 243.
Clouds, on the conductivity of, dispersed from an arc, 1266.
Cobalt, on the absorption spectrum of, 451.
Colloidal particles, on the adsorption of ions on, 32.
Combridge (J. T.) on the field of a thick spherical shell on Einstein's theory of relativity, 276.
Compression, on the ignition of gases by sudden, 1094.
—— tests on circular cylinders, on the determination of Young's modulus from, 463.
Condenser, on the resistance of a, at radio frequency, 428.
Crehore (Dr. A.) on the forces of chemical affinity, 786.
Critchlow (J.) on a supposed relativity method of determining the size of a gravitating particle, 67.
Critical increment of chemical action, on the nature of the, 606.
Crystal analysis, on results of, 1151.
Crystal-molecule, on the symmetry of the, 289.
Crystal structure, on, 786.
Crystalloids, on the separation of, by dialysis, 385.
Crystals, on the reflexion of X-rays by, 897, 1009.
Current in an electrically maintained tuning-fork circuit, on the wave-form of the, 738.
Currents, on discharge, in well-exhausted tubes, 609.

Curtis (Dr. W. E.) on new series in the secondary hydrogen spectrum, 695.
D-lines, on models for the, 181.
Darwin (Prof. C. G.) on mechanical models for the Zeeman effect, 161; on the intensity of reflexion of X-rays by crystals, 897.
Datta (S. K.) on the determination of surface-tension by the method of ripples, 1252.
David (Prof. W. T.) on the pressures developed on explosion of gaseous mixtures, 334.
Davis (N. R.) on the quantitative theory of induction heating, 768.
De Foe (O. K.) on the separation of the modified and unmodified scattering coefficients of X-rays, 711.
Delta-rays, on the, produced by alpha-rays, 1.
Dennison (Dr. D. M.) on the analysis of certain molecular spectra, 195.
Dialysis, on the separation of crystalloids by, 385.
Diamond lattice, on a model of the, 813.
Dielectric and other physical properties of non-metallic elements, on the connexion between, 225.
—— constants of benzene solutions, on the, 1035.
Diffraction phenomena, on the Fraunhofer, for a polygonal aperture, 132.
Dimensional analysis, on, 257, 1145.
Disk, on the effect of axial restraint on the stress in a rotating, 1236.
Donnan's membrane equilibrium theory, on, 32.
Dynamic balance, on the determination of minima maxima forces in, 635.
Earth, on the surface history of the, 923, 932.
Earth's atmosphere, on the energy in the, 523.
Ehrenfest-Afanassjewa (Mrs. T.) on dimensional analysis and the theory of similitudes, 257.
Einstein's theory of relativity, on the field of a thick spherical shell on, 276.
Electric conductivity, on the, of clouds dispersed from an arc, 1266.
Electric discharge, on gas flow and pressure changes in gases under, 482.
Electrical resistance of a condenser at radio frequency, on the, 428.
Electrification of two intersecting planes, on the, 337.
Electrode potential, on Nernst's theory of, 641.
Electromotive force of a photo-active cell on the variation of the, 532.
Electron structure, on models of, 13.
Electrons, on the emission of, under intense electric fields, 609.
Elements, on the non-metallic, 225.
——, on the X-ray spectra of the lower, 312.
Emeléus (K. G.) on the delta rays produced by alpha-particles in different gases, 1.
Emulsions, on the optical properties of chromatic, 321.
End point, on a simple method of determining the, 496.
Entropy, on the absolute value of, 279; on the, of radiation, 890.
Erythritol, on an X-ray examination of, 289.
Explosion of gaseous mixtures, on the pressures developed on the, 334.
Fairweather (Dr. D. A.) on the melting-points of the normal saturated dibasic acids, 944.
Fatigue fractures, on the propagation of, 71.
Fine structures of complex mercury lines, on the, 977.
Fizeau's experiment, on the significance of, 1198.
Flaw, on the concentration of stress round a spherical, 71.
Fluorescent electrolyte, on the E.M.F. of a cell containing a, 532.
Fluorine, on the scattering power of, for X-rays, 1202.
Fluorspar, on the intensity of reflexion of X-rays by, 897.
Foster (P. F.) on the determination of minima maxima forces in problems of dynamic balance, 635.
Fowler (R. H.) on the statistical mechanics of assemblies of ionized atoms and molecules, 845.

Frameworks, on the application of Saint-Venant's principle to, 243; on the effect of curved members upon the elastic properties of a, 254.
Fraser (R.) on the refractive index of gases and vapours in a magnetic field, 885.
Fraunhofer diffraction phenomena, on the, for a polygonal aperture, 132.
Frayne (Dr. J. G.) on the absorption spectra of the vapours of Zn, Cd, Pb, Sn, Bi, and Sb, 732.
Free (O.) on the zirconium in Colorado pitchblende, 950.
Furnace, on the energetics of an induction, 768.
Galvanometers, on the sensibility of, 827.
Gas, on the effect of the presence of an indifferent, on the concentration and activity of a vapour, 561.
Gaseous mixtures, on the pressures developed on explosion of, 334.
Gases, on the adsorption of, by activated charcoal, 109, 659, 1042; on gas flow and pressure changes in, under electric discharge, 482; on the optical anisotropy of some inorganic, 491; on the variation of the thermal conductivity of, with pressure, 593; on the refractive index of, in a magnetic field, 885; on the ignition of, by sudden compression, 1094.
Geological Society, proceedings of the, 558, 700, 896.
—— time, on estimates of, 1055.
Geometrical problems, on the mechanical solution of some, 783.
Germanium in a British mineral, on, 1007.
Ghosh (P. N.) on the determination of surface-tension by the method of ripples, 1252.
Ghosh (R. N.) on the choice of striking point in the pianoforte string, 875.
Gibbs' adsorption equation, on an experimental verification of, 641.
Gossling (B. S.) on the emission of electrons under the influence of intense electric fields, 609
Gough (H. J.) on the concentration of stress in a spherical flaw, and on the propagation of fatigue fractures, 71.
Gravitating particle, on a supposed relativity method of determining the size of a, 67.
Gravitational field, on models of the, 13.
Green (W. G.) on the effect of axial restraint on the stress in a rotating disk, 1236.
Gregory (Dr. H.) on the variation of the thermal conductivity of gases with pressure, 593.
Hassé (Prof. H. R.) on Langevin's theory of ionic mobility, 139.
Helium, on the production of delta-rays in, 1.
—— atom, on the, 29.
Holmes (Dr. A.) on estimates of geological time, 1055.
Howland (R. C. J.) on the vibrations of rods and shafts with tension or end-thrust, 674.
Hydrogen, on the production of delta-rays in, 1; on the absorption of, in potassium vapour arcs, 97; on the solubility of, in tin and aluminium at high temperatures, 510; on the crystal structure of solid, 786; on the scattering of positive rays by, 961; on the adsorption of, by activated charcoal, 1042.
—— atoms, on the, 17; on the time of excitation of, 1082.
—— over-potential at a mercury cathode, on, 1282.
—— spectrum, on new series in the secondary, 695.
Hypergeometric functions, on the roots of, 273.
Ignition of gases by sudden compression, on the, 1094.
Induction heating, on the quantitative theory of, 768.
Integrals, on the evaluation of, by L-functions, 308.
Ionic mobility, on Langevin's theory of, 139.
Ionization equilibrium, on the influence of radiation on, 1025.
—— potentials, on, 726.
—— produced by spraying, on the, 417.
Ionized atoms and molecules, on the statistical mechanics of assemblies of, 845.
Iron, on the A_3 and A_4 transformations in pure, 996.

Iron, on the water-spark absorption spectrum of, 433, 704.
Ising (G.) on a natural limit for the sensibility of galvanometers, 827.
J phenomenon, on the, 542.
Jackson (Dr. L. C.) on the orientation of the oxygen molecule in a magnetic field, 1193.
James (R. W.) on the intensity of reflexion of X-rays by crystals, 897; on the scattering powers of calcium and fluorine for X-rays, 1202.
Jauncey (Prof. G. E. M.) on the separation of the modified and unmodified scattering coefficients of X-rays, 711.
Jeffreys (Dr. H.) on Professor Joly's theory of earth history, 923.
Kahlenberg (Prof. L.) on the separation of crystalloids by dialysis, 385.
Kaye (Dr. G. W. C.) on an improved all-metal mercury-vapour pump, 349.
Kempe (H. R.) on the mechanical solution of some geometrical problems, 783.
L-functions, on the, 304.
Langevin's theory of ionic mobility, on, 139.
Laws (Dr. B. C.) on lines of maximum stress in mild steel plates, 1039.
Lead, on the absorption spectrum of the vapour of, 732.
Light, on the magnetic gyration of, 178; on the propagation of, in emulsions, 324.
Line, on the generalized artificial, 553.
Linear relation connecting three variables, on the best, 378.
Liquids, on molecular changes in, 1121.
Logarithmic decrement, on the variation of, with amplitude and viscosity of metals, 1074.
Lorenz (E. J.) on the positive photoelectric emission and the reality of the sub-electron, 499.
Lunnon (R. G.) on gas flow and pressure changes in gases under electric discharge, 482.
McAulay (A. L.) on hydrogen overpotential at mercury cathode, 1282.
McHaffie (I. R.) on the effect of the presence of an indifferent gas on the concentration and activity of a vapour, 561.
Mackenzie (Miss G. I.) on the superposition of X-rays and on scattering, 542.
McPetrie (J. S.) on the time of excitation of hydrogen atoms, 1082.
Magnetic field, on the refractive index of gases and vapours in a, 885.
—— gyration of light, on the, 178.
Majumdar (K.) on the absorption spectra of aluminium and cobalt, 451.
Melting-points, on the, of the normal saturated dibasic acids, 944.
Menges (C. L. R. E.) on the signification of Fizeau-Zeeman's experiments, 1198.
Mercury cathode, on hydrogen overpotential at a, 1282.
—— lines, on the fine structure and Zeeman effect of complex, 977.
——, on the adsorption by, of its own ions, 641; on a method for exciting the spectrum of, 752.
Mercury-vapour pump, on an all-metal, 349.
Metals, on a method for exciting the spectra of certain, 752; on the variation of logarithmic decrement with viscosity of, 1074.
Models of electron structure, quantum action, and the gravitational field, on, 13; of the Zeeman effect, on, 161.
Molecular changes in vapours and liquids, on, 1121.
—— spectra, on the analysis of certain, 195.
Molecules, on the statistical mechanics of assemblies of ionized, 845.
Morton (Dr. R. A.) on refractivity, ionization potentials, and absorption spectra, 726.
Morton (Prof. W. B.) on the electrification of two intersecting planes, 337.
Newman (Prof. F. H.) on the low voltage arc in cæsium vapour, 705; on enhanced lines produced by the interruped arc in sodium and potassium vapours, 721; on the sodium arc in a vacuum, 940.
Nitrogen, on the adsorption of, by activated charcoal, 121, 1042.
Nitrogen, on the production of the spectrum of, in the presence of neon, 405.

Nolan (Dr. P. J.) on the ionization produced by spraying water, 417.
Nuttall (J. M.) on the beta-rays associated with scattered X-rays, 1217.
Odell (N. E.) on the geology of Central Spitzbergen, 700.
Oldham (R. D.) on the depth of origin of earthquakes, 896.
Optical properties of chromatic emulsions, on the, 321; anisotropy of inorganic gaseous compounds, on the, 491.
Oxygen, on the adsorption of, by activated charcoal, 123; on the orientation of the molecule of, in a magnetic field, 1193.
——, on the production of the spectrum of, in the presence of neon, 405.
Partington (Prof. J. R.) on the dielectric constants of benzene solutions, 1035.
Photoactive cell, on the E.M.F. of a, 532.
Photoelectric emission, on the positive, 499.
Piaggio (Prof. H. T. H.) on a supposed relativity method of determining the size of a gravitating particle, 67.
Pianoforte string, on the choice of striking point in the, 875.
Pippard (Prof. A. J. S.) on the application of Saint-Venant's principle to frameworks having redundant bracing members, 243; on the effect of curved members on the elastic properties of a framework, 254.
Pitchblende, on the zirconium in Colorado, 950.
Planes, on the electrification of two intersecting, 337.
Pleochroic haloes, on, 1069.
Population, on the hypothetical infinite, of theoretical statistics, 670.
Positive rays, on the scattering of, by hydrogen, 961.
Potassium vapour, on enhanced lines produced by the interrupted arc in, 721.
—— —— arcs, on the absorption of hydrogen in, 97.
Powellite, on the crystal of, 1177.
Pump, on an all-metal mercury-vapour, 349.
Pye (D. R.) on the ignition of gases by sudden compression, 1094.
Quantum action, on models of, 13.
—— mechanics, note on, 1114.
Quotient theorem, on the application of the rigorous, 748.
Radiation, on the pressure of, 584; on the entropy of, 890; on the influence of, on ionization equilibrium, 1025; note on, 1111.
Radium C, on the efficiency of beta-ray recoil of radium B from, 835.
Ramanathan (Dr. K. R.) on the optical anisotropy of some inorganic gaseous compounds, 491.
Randall (J. T.) on the scattering powers of calcium and fluorine for X-rays, 1202.
Reaction constant equation, on the, 496.
Refractive index, on the, of gases and vapours in a magnetic field, 885.
Refractivity, on, 726.
Relativity method of determining the size of a gravitating particle, on a, 67.
——, on the field of a thick spherical shell on the theory of, 276.
Relton (F. E.) on the determination of Young's modulus from compression tests on circular cylinders, 463.
Riding (R. W.) on refractivity, ionization potentials, and absorption spectra, 726.
Rigorous quotient theorem, on the application of the, 748.
Rinde (Dr. H.) on the adsorption of ions on colloidal particles, 32.
Ripples, on the determination of surface-tension by the method of, 1252.
Robertson (Prof. J. K.) on a method for exciting the spectra of certain metals, 752.
Rock-salt, on the intensity of reflexion of X-rays by, 897.
Rods, on the vibrations of, with tension on end-thrust, 674.
Rotating disk, or the effect of axial restraint on the stress in a, 1236.
Rowe (H.) on the adsorption of gases by activated charcoal, 109 659, 1042.
Ruark (A. E.) on the fine structure and Zeeman effect of complex mercury lines, 977.
Rule (J. F. J.) on the dielectric constants of benzene solutions, 1035.

Rule (W.) on the variation of the E.M.F. of a photoactive cell, 532.
Rusk (Dr. R. D.) on the absorption of hydrogen in potassium vapour arcs, 97.
Rutile, on the crystal of, 1169.
Saha (Prof. M.) on the absolute value of entropy, 279; on the entropy of radiation, 890; on the influence of radiation on ionization equilibrium, 1025.
Saint-Venant's principle, on, 243.
Sandford (Dr. K. S.) on the geology of North-East Land, 702.
Sato (Dr. K. S.) on the A_3 and A_4 transformations in pure iron, 996.
Scheelite, on the crystal of, 1177.
Schlapp (Dr. R.) on the reflexion of X-rays from crystals, 1009
Schofield (R. K.) on an experimental verification of Gibbs' adsorption equation, 641.
Scutt (W.) on germanium in a British mineral, 1007.
Searle (V. H. L.) on the wave form of the current in an electrically maintained tuning-fork circuit, 738.
Sedgwick (W. F.) on the second law of thermodynamics, 1286.
Shafts, on the vibrations of, with tension or end-thrust, 674.
Shell, on the field of a thick spherical, on Einstein's theory of relativity, 276.
Similitudes, on the theory of, 257.
Smith (Dr. A. W.) on the absorption spectra of the vapours of Zn, Cd, Pb, Sn, Bi, and Sb, 732.
Smith (R. C.) on the reaction constant equation, 496.
Sodium arc in a vacuum, on the, 940.
—— D-lines, on models for the, 181.
—— vapour, on enhanced lines produced by the interrupted arc in, 721; on the refractive index of, in a magnetic field, 885.
Sogani (Prof. C. M.) on the optical properties of chromatic emulsions, 321.
Solids, on the surface-tension of, 1258.
Southwell (R. V.) on the concentration of stress in a spherical flaw, and on the propagation of fatigue fractures, 71.
Spark gap, on the theory of the three-point, 353.
Sparking potential, on the relation between temperature and minimum, 219.
Spectra, on the analysis of certain molecular, 195; on the, of carbon, oxygen, and nitrogen in the presence of neon, on the production of, 405; on absorption, 726; on the absorption, of the vapours of Zn, Cd, Pb, Sn, Bi, and Sb, 732; on a method for exciting, of certain metals, 752.
Spectrum of iron, on the water-spark absorption, 433, 704; on the absorption, of aluminium and cobalt, 451.
Spencer (Dr. E.) on occurrences of spherulitic siderite in sediments, 559.
Srinivasan (N. G.) on the optical anisotropy of some inorganic gaseous compounds, 491.
Statistical mechanics of assemblies of ionized atoms and molecules, on the, 845.
Statistics, on the hypothetical infinite population of theoretical, 670.
Steel, on the propagation of fatigue fractures in, 86; on lines of maximum stress in plates of, 1039.
Stress, on the concentration of, in a spherical flaw, 71; on lines of maximum, in steel plates, 1039.
——, on the effect of axial restraint on the, in a rotating disk, 1236.
Sub-electron, on the reality of the, 499.
Subrahmaniam (G.) on the variation of logarithmic decrement with amplitude and viscosity of metals, 1074.
Sur (N. K.) on the water-spark absorption spectrum of iron, 433, 704; on the absorption spectra of aluminium and cobalt, 351.
Sur (R. K.) on the absolute value of entropy, 279; on the entropy of radiation, 890; on the influence of radiation on ionization equilibrium, 1025.
Surface history of the earth, on the, 923, 932.
Surface-tension, on the determination of, by the method of ripples, 1252; on the, of solids, 1258.
Sutton (T. C.) on the nature of the critical increment of chemical action, 606.

Swann (Prof. W. F. G.) on the pressure of radiation, 584.
Teegan (J. A. C.) on a thermionic valve method of measuring the velocity of air-currents in pipes, 1117.
Temperature and minimum sparking potential, on the relation between, 219.
Thermal conductivity of gases, on the variation of, with pressure, 593.
Thermodynamics, on the second law of, 1286.
Thomson (Prof. G. P.) on the scattering of positive rays by hydrogen, 961.
Thoræus (R.) on the X-ray spectra of the lower elements, 312.
Thorium minerals, on, with reference to estimates of geological time, 1055.
Thornton (Prof. W. M.) on models of electron structure, quantum action, and the gravitational field, 13.
Three-point gap, on the theory of the, 353.
Time and chance, on, 1106.
Tin, on the solubility of hydrogen in, at high temperatures, 510; on the absorption spectrum of the vapour of, 732.
Tizard (H. T.) on the ignition of gases by sudden compression, 1094.
Tuning-fork circuit, on the wave-form of the current in an electrically maintained, 738.
Umbral notation, note on, 304.
Uranium haloes, on, with reference to estimates of geological time, 1055.
Vapour, on the effect of the presence of an indifferent gas on the concentration and activity of a, 561.
Vapours, on the refractive index of, in a magnetic field, 885; on molecular changes in, 1121.
Variables, on certain functions of two, 304; on the best linear relation connecting three, 378.
Vegard (Prof. L.) on results of crystal analysis, 1151.
Vibrations of rods and shafts with tension or end-thrust, on the, 674.
Viscometer, on the air-bubble, 395.
Walmsley (H. P.) on the conductivity of clouds dispersed from an arc, 1266.
Water, on the ionization produced by spraying, 417; on the evacuation of, 762.
Water-spark absorption spectrum of iron, on the, 433, 704.
Whipple (F. J. W.) on the best linear relation connecting three variables, 378.
Williams (E. J.) on the beta-rays associated with scattered X-rays, 1217.
Witmer (Dr. E. E.) on the Fraunhofer diffraction phenomena for a polygonal aperture, 132.
Wrinch (Dr. D. M.) on the roots of hypergeometric functions, 273.
Wrinch (H. E. H.) on the roots of hypergeometric functions, 273.
Wynn-Williams (C. E.) on the theory of the three-point gap, 353.
X-ray examination of *i*-erythritol, on an, 289.
—— spectra of the lower elements, on the, 312.
—— spectrum, on the distribution of energy in the continuous, 50.
X-rays, on the beta-rays associated with scattered, 1217.
——, on the superposition of, 542; on the separation of the modified and unmodified scattering coefficients of, 711; on the reflexion of, by crystals, 897, 1009; on the scattering powers of calcium and fluorine for, 1202.
Young's modulus, on the determination of, from compression tests on circular cylinders, 463.
Zeeman effect, on mechanical models for the, 161; on the, of complex mercury lines, 977.
Zeeman's experiment, on the significance of, 1198.
Zinc, on the absorption spectrum of the vapour of, 732; on a method for exciting the spectrum of, 752.
Zircon, on the crystal of, 1158.
Zirconium, on the, in Colorado pitchblende, 950.

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44940